THE PORPHYRINS AND INTERSTELLAR DUST

Dr. Fred M. Johnson, Manager
Quantum Electronics Department

ELECTRO-OPTICAL SYSTEMS, INC.

A XEROX COMPANY

SECTION 1

THE PORPHYRINS

On the basis of spectral comparisons of all the known hydrocarbon and cyclic [H, C, N] spectra, porphyrins seem to have three of the properties which are necessary but not sufficient for making them candidates for interstellar dust particles. These are the positions of the absorption bands, particularly the strong Soret band, their stability to uv radiation, and a large variety of available compounds of which a number have absorption bands very close to the interstellar diffuse absorption lines. The spectral line width of these bands will be discussed, in particular the noticeable sharpening of the spectrum in the pyridine haemochrome series compounds. The important properties of these porphyrin compounds will first be outlined including the definitions of structural formula. Section 2 will review the theoretical aspects underlying the absorption spectra.

1.1 STRUCTURE

The porphyrins are derived formally from porphin by substitution of some or all of the hydrogen atoms 1 to 8 by various side-chains. The porphin macrocycle is highly conjugated, and a number of resonance forms can be assigned. The characteristic properties of all their derivatives are intensely colored absorption bands whose molar extinction coefficients are of the order of 100,000. Table I, taken from Falk, shows the structural formulas and is a table of the derivative of these compounds by substituents on positions 1 to 8 to various side-chains. The molecule can be regarded essentially as planar, with a diameter of approximately 8.5Å and a thickness of approximately 4.7Å; there are deviations from this planarity, however. The basic structure is a microcyclic tetrapyrrole structure, first suggested by Kuster in 1912. The shape of the molecule is different in solution and in the crystalline state.

TABLE I

EFFECT OF SUBSTITUENTS ON WAVELENGTH AND
TYPE OF VISIBLE SPECTRUM OF PORPHYRIN ESTERS

|	Substituent at Position (see Fig. 1)		Band I (dioxan) (mμ)	Spectral Type
Deuteroporphyrin IX	2	4		
	H	H	618	Aetio
	C_2H_5	C_2H_5	620	Aetio
M —— 2 M —— 4	$CH{=}CH_2$	$CH{=}CH_2$	630	Aetio
	H	CHO	640	Rhodo
	H	C$=$NOH	630	Aetio
M —— P P —— M	CHO	$CH{=}CH_2$	641	Rhodo
	C$=$NOH	$CH{=}CH_2$	635.5	Aetio
	CHO	CHO	650	Aetio
	C$=$NOH	C$=$NOH	639	Aetio
	$COCH_3$	$COCH_3$	639	Aetio
	C($=$NOH)CH_3	C($=$NOH)CH_3	625	Aetio
Pyrroporphyrin XV	6			
	H		620	Aetio
	$CH{=}CH_2$		624	Aetio
M —— E M —— E	CHO		635.5	Rhodo
	$COCH_3$		632	Rhodo
	COC_6H_5		627	Rhodo
M —— P 6 —— M	$COOCH_3$		632	Rhodo
	$CH{=}CHCOOCH_3$		624.5	Rhodo
2-Desethylpyrro-porphyrin XV	2	6		
	C_2H_5	$COOCH_3$	632	Rhodo
M —— 2 M —— E	$CH{=}CH_2$	$COOCH_3$	638.5	Rhodo-oxorhodo
	$COCH_3$	$COOCH_3$	637	Oxorhodo
M —— P 6 —— M	C($=$NOH)CH_3	$COOCH_3$	631	Rhodo
	$COCH_3$	$COCH_3$	637	Oxorhodo
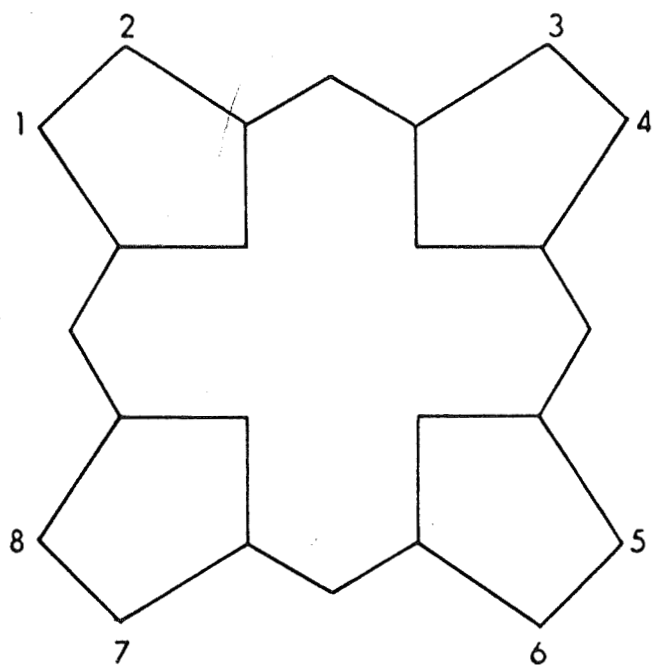
Figure 1. Basic Porphyrin Structure

73628101

(The chief reason why such an extensive survey as shown in this report, is necessary is based on the fact that not all the required spectroscopic information is available in order to make a fair comparison with the interstellar dust particles. As will be pointed out in a number of places in this report, the interstellar dust particles are presumed to have dimensions of the order of 10^{-5} cm and are very finely dispersed throughout the interstellar medium with temperatures of the order of 20°K. Since it is extremely difficult to simulate these conditions in the laboratory, a range of physical phenomena will have to be examined and extrapolations made. Thus when absorption data are taken in liquids, the effects of the solvent must be evaluated as well as pH, dryness, concentration, etc.)

Familiar compounds belonging to the porphyrin group are chlorophyll, haem, and vitamin B-12. Their importance in nature makes their study important in the biological field. It has resulted in a considerable literature. Note that the location at the center of the structure could be either metal-free or contain a metal such as Fe or Mg. The protoporphyrin and protohaem structures are shown in Fig. 2. A comparison of the chlorophyll and haem structures is shown in Fig. 3.

The isomerism in porphyrins is discussed briefly. There are three substituent groups. As in protoporphyrin, 15 isomers are possible. Protoporphyrin IX is systematically related to aetioporphyrin III and their respective porphyrinogens, which are the biosynthetic precursors of the biologically important protoporphyrin IX and protohaem IX. Every porphyrin and metalloporphyrin known to have a metabolic function is modelled on this general pattern of side-chain substitution including the prosthetic groups of all the known haemoproteins, the chlorophylls, and vitamin B-12 (see p. 15, Falk).
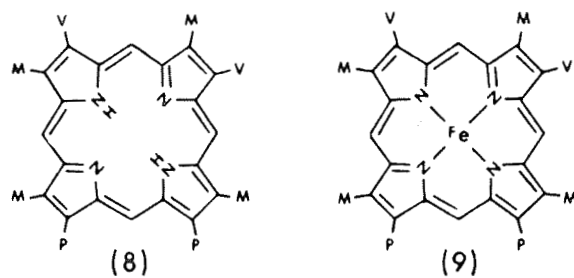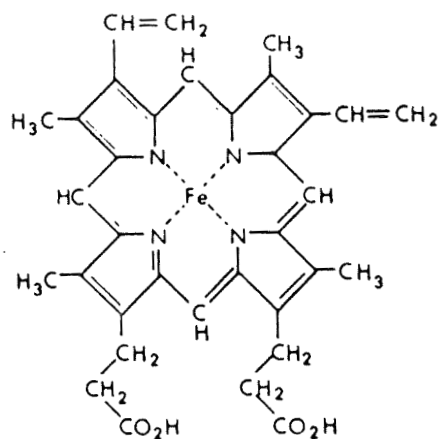
(8) PROTOPORPHYRIN IX   (9) PROTOHAEM IX

Figure 2.   Structures of Protoporphyrin
IX and Protohaem IX

CH=CH₂ CH₃ CH=CH₂ CH₃
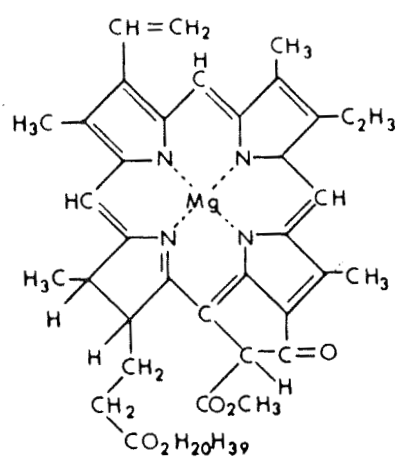
CHLOROPHYLL   HEMIN

Figure 3. Structures of Important Porphyrins

1.2 STABILITY

The esters and metal complexes of the porphyrins melt in the region
200-300°C often without decomposition. Some porphyrins and their metal
complexes may be sublimed unchanged in high vacuum in the range 200-
300°C; phthalocyanine sublimes unchanged at 550°C. The porphyrin nu-
cleus is stable to concentrated sulfuric acid.

The appearance of porphyrins in natural environments and in petroleums
is evidence of their chemical stability. When haematin and chloropor-
phyrins are exposed to geologic environments, their metal atoms are
usually lost; not so, however, their skeleton structure, metal-free
porphyrins being formed. In time, other atoms such as nickel and van-
adium, substitute for the iron and magnesium, yielding very stable com-
plexes. It is these forms of the porphyrins that are usually found in
old sediments, particularly since they are very soluble in petroleums
where they are found abundantly. These porphyrins have been found in
specimens that are at least half a billion years old. Treibs reported
finding metalloporphyrins in 66 crude oils, 9 asphalts, 70 bituminous
oil shales, and 17 coals, the oldest samples being found in Cambrian
shales. The fact that these porphyrins are found in conjunction with
petroleum products is evidence for their organic origin (Phillip H.
Abelson).

1.3 STABILITY TO LIGHT

The porphyrins do react to light since they have absorption bands in
the uv and visible region. In fact, it is their light sensitivity which
makes these compounds useful in the field of biology, e.g., photo-
synthesis. Of particular significance is the fact that an absorption
band in the ultraviolet at 2800Å exists for the porphyrins. Most
of the porphyrins fluoresce on irradiation in the ultraviolet. This

uv absorption allows for stability of these compounds since their energy can be dissipated in a cascade process via fluorescence (H. Linschitz, private communication). A great deal of work has been done on fluorescent excitation and emission spectra, the conditions for their occurrence depending on the pH, solvent, and impurities. The excitation maxima are necessarily close to the absorption maxima in both the Soret and visible regions, but usually only one emission is found at a little longer wavelength than that of the absorption band. No instances are known of fluorescence in a porphyrin complex with a transition metal ion. On the other hand, some metalloporphyrins containing ions that have no unpaired electrons (magnesium, zinc, cadmium, tin, barium), while not fluorescing in anhydrous, nonpolar solvents, give fluorescent compounds in the presence of polar ligands. The fluorescence spectra of chlorophyll and pheophytins are no doubt due to the presence of water molecules coordinated to their magnesium atoms.

1.4 SPECTRA OF THE PORPHYRIN MOLECULES

Some general comments on the spectra will be given in this section. Theoretical details are discussed in Section 3. Some of the main points are as follows: Factors which encourage an increase in the π-electron density of the periphery of the porphyrin nucleus cause shifts along the wavelengths in the absorption bands, and the fluorescent emission band is present. Shifts to longer wavelengths are found as the electron-attracting power of side-chains increases and as the stability of porphyrin chelates with different metal ions decreases (as the covalent component in the bonding decreases).

Among further complexes of iron porphyrins (Fe(II) porphyrins), the low-spin complexes formed by π-bonding ligands have sharp absorption bands and absorb at shorter wavelengths than the high-spin complexes formed by saturated ligands. An absorption band at 6300Å is ascribed

to a charge transfer band found in the high-spin but not in the low-spin complexes. Note that a strong interstellar diffuse absorption line at 6284 might correspond to this charge transfer band. For the porphyrin chelates with different metal ions, the shift of absorption to longer wavelength, corresponding to a decrease in stability, is associated with a decrease in the ratio of the intensity of band I to band II. The nature and distribution of the side-chains determine the ratios of intensity of the four main visible bands of porphyrins in neutral solvents (Falk, p. 72).

The absorption of porphyrins in the so-called Soret band is most characteristic of these compounds and was one of the most important clues for its suggested identification for the interstellar grains, since the interstellar absorption band at 4430 is likewise the strongest observed feature. Since the Soret band varies from 4000 to 4500Å for these compounds, it remains to choose among the hundreds of compounds which showed absorption close to these interstellar diffuse lines. Such comparisons are discussed in more detail in Section 4. The major extinction of the Soret band is between 200,000 and 500,000, usually 10 to 20 times as intense as the strongest of the visible bands. This Soret band is found in all tetrapyrroles in which the nucleus is fully conjugated, including porphyrins, metalloporphyrins, and haemaproteans. It is present of course in chlorophyll and vitamin B-12. The effect of solvents on the position of the band requires detailed study since changes of intensity as well as the wavelength occur with different solvents. The effect of substitutions on the position of the wavelength for certain porphyrin esters is shown in Table I.

It is interesting to note that certain lines in the pyridine haemochrome spectrum are sharpened considerably, presumably due to a change from the dimeric to the monomeric species. Similar changes are believed to occur also in the sharpening of the lines in the ferroporphyrin spectrum. The low-spin Fe-II porphyrin complexes have sharper absorption

bands at shorter wavelengths than the high-spin complexes. This is due to the interaction of electrons in the third t_{2g} orbital of low-spin iron complexes with π-orbitals of the ligand nitrogen atoms (see Falk, p. 82 "Theory of the Porphyrin Spectra"). One may consider the porphyrin molecule as consisting of a framework of atoms held together by two-electron (σ) bonds and by the remainder of the valence electrons (the π-electrons), which occupy molecular orbitals extending over the whole framework. The resultant strong delocalization of the π-electrons is responsible for the aromatic character of the porphyrin nucleus and results in small enough energy differences between the highest occupied orbital and the lowest vacant orbital for transitions between these to give rise to absorption bands in the visible and near-ultraviolet region of the spectrum (Falk, p. 90).

In general there are four bands in the porphyrin molecules in neutral solvents aside from the Soret band. Some believe that the visible bands are really two pairs of bands which would be superimposed if the porphyrin nucleus were strictly square and uniformly substituted. X-ray analysis of the closely similar phthalocyanine molecule has shown this structure to be slightly distorted from the square configuration. In cases where this distortion is not present, such as in the porphyrin dianion and dication and in porphyrin chelates with divalent metal ions, two visible bands only are found.

The observed bands arise due to transitions between filled orbitals of A_{2u}-type symmetry and vacant E_g-type orbitals. The bands are associated with electronic displacement towards the periphery which may be either along or perpendicular to the axis of the two hydrogen atoms (which are on opposite pyrrole nitrogens). Because bands I and III are for a (0-0) vibrational transition, which is classed as forbidden, intensities will depend very much more on any loss of symmetry in the porphyrin molecule than will bands II and IV, which are interpreted as

(0-1) allowed vibrational bands. Substitution of alkyl groups or carboxyl groups will not affect the symmetry of the molecules. Greater distortion, however, is observed on substitution of a peripheral hydrogen atom by a group such as -CHO, -COCH$_3$, or -COOCH$_3$.

The Soret band is thought to be due to transition of an electron in an A_{1u} orbital in which it is confined to the carbon atoms of the pyrrole ring to an E_g orbital, which is one of a pair of equal energy, strongly polarized along and perpendicular to the axis of the two NHs. Spectroscopic effects may be explained by the ease with which the movement of electrons towards the periphery of the porphyrin plane can be facilitated. Gouterman has shown that the less electronegative the metal, the greater the intensity of the visible bands of the metalloporphyrins and the longer their wavelength. Similarly, strongly electron-attractive substituents of the porphyrin nucleus cause shifts to the longer wavelength for all the bands of the porphyrins.

THEORY

In this section we wish to summarize some of the theoretical discussions
that have been given by various authors. No claim is made here for com-
pleteness; the various theories are reported and described mainly to
clarify and illuminate the situation. One has to recognize that a great
deal of overlap occurs among various authors and that different inter-
pretations are possible. As can be seen in the bibliography, great con-
tributions to the theory were made by J. R. Platt, M. Gouterman and their
associates. First we wish to quote a paper by Gurinovich, et al.

> "Group theory permits us to classify the electronic
> and vibrational states of molecules according to the
> transformation properties of the wave functions with
> respect to various symmetry operations. The π-elec-
> trons have the peculiarity that their orbitals are
> necessarily antisymmetric with respect to the opera-
> tion of reflection in the plane of the molecule.
> This limits the number of possible types of orbitals,
> and hence, of states. In particular, for symmetry
> D_{4h} the only possible orbitals are a_{1u}, a_{2u}, b_{1u},
> b_{2u}, and e_g.* For symmetry D_{4h}, the only possible
> states permitted by group theory are the nondegener-
> ate even states A_{1g}, B_{1g}, A_{2g}, B_{2g}, and the doubly-
> degenerate odd state E_u. When the symmetry is lowered
> to D_{2h}, the E_u state splits in two: B_{2u} and B_{3u}, while
> the even states change symbols: A_{1g} and B_{1g} go over
> into A_{1g} and A_{2g}, while B_{2g} goes over into B_{1g}. Fig-
> ure 4 illustrates what has been said. The signs "+"
> and "-" indicate the sign of the wave function.
>
> The ground electronic state of the porphyrins, as
> with other classes of compounds, must be totally-
> symmetric (A_{1g}). Using the table of direct products,**
> and taking into account the possible types of sym-
> metry of π-electron states, we can easily derive the

---

*See, e.g., Longuet-Higgins, Rector, and Platt, J. Chem. Phys. 18,
1174 (1950)

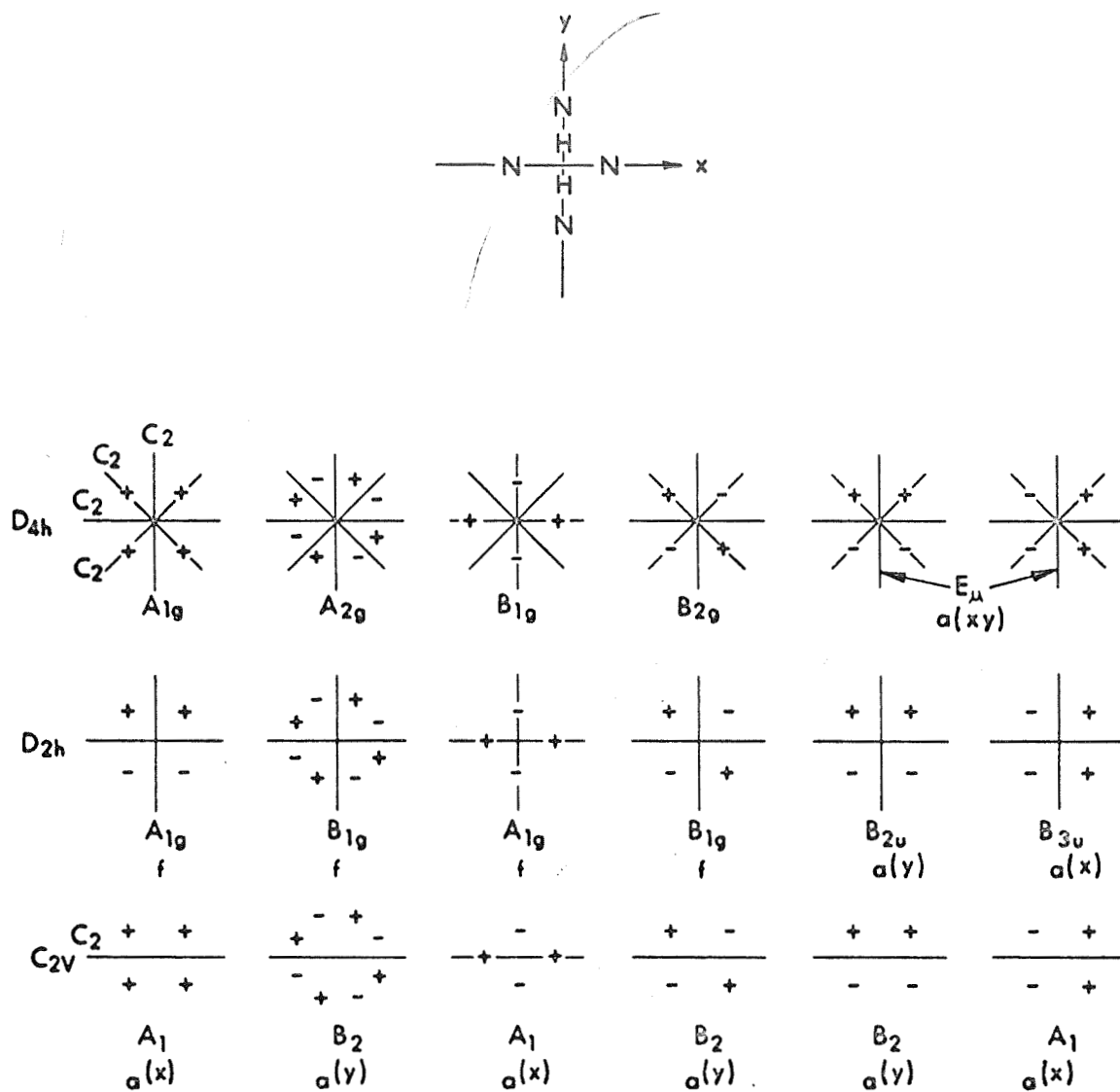**See, e.g., H. Sponer and E. Teller, Revs. Mod. Phys., 13, 75 (1941)

Figure 4. Symmetry Types of the Possible π-Electron States of the Porphin Ring

following selection rules for the porphyrins. The only transitions allowed in absorption are those to the degenerate E_u states (for symmetry D_{4h}) and to the B_{2u} and B_{3u} states (for symmetry D_{2h}). The moments of the transitions A_{1g}—B_{2u} and A_{1g}—B_{3u} are mutually perpendicular. Correspondingly, Fig. 4 indicates the states for which transition from the ground state is allowed by the letter a, and those forbidden by the letter f. The polarizations of the transitions are also indicated there. In the case of symmetry C_{2v} (dihydroporphin), all the transitions forbidden for symmetry groups D_{4h} and D_{2h} are allowed, in line with the absence of a center of symmetry.

The experimental data indicate that the allowed transition in the metalloporphyrins and doubly-charged porphyrin ions corresponds to the Soret band. According to what has been said above, this band must be assigned to the transition A_{1g}—E_u. The small change in the form of this band when the symmetry is lowered means that the states B_{2u} and B_{3u} resulting from splitting of the doubly-degenerate E_u state are close in energy. Apparently, the Soret band of the neutral porphyrin molecules corresponds to two allowed transitions which are close in frequency, and have mutually-perpendicular orientations, in agreement with the polarization spectrum.

In the metalloporphyrins and the porphyrin cations, the lowest excited state is also doubly degenerate. Correspondingly, the long-wavelength transition $(A_{1g}$—$E_u)$ here should be allowed by the selection rules for symmetry D_{4h}. Hence, the low intensity of band I in this case cannot be explained by a selection rule forbidding the transition on grounds of symmetry, and we must have recourse to other arguments. In particular, Simpson used for this purpose the idea of transitions being "forbidden by the angular momentum." Without going into an analysis of the views of various authors on this problem, we should note that in annular conjugated systems there are factors which greatly weaken transitions which are not forbidden by symmetry. Analogous arguments can also be adduced for symmetry D_{2h}; the relatively low intensity of bands I and III may be due to the same factors.

Here, the assumption that the forbidden character does not involve the symmetry of the molecules is also confirmed by a comparison of the absorption and luminescence spectra of porphin and tetrazaporphin. The intense absorption bands of tetrazaporphin are related to band I and III of porphin, since successive substitution of the bridge carbon atoms by nitrogen atoms increases the intensity of these bands, but hardly alters their positions. When a metal is introduced, the intense absorption bands of tetrazaporphin belonging to the allowed transitions A_{1g}—B_{2u} and A_{1g}—B_{3u}, whose oscillators are mutually-perpendicular, merge into one band having planar oscillator. This analogy shows that the electronic excited states do not differ in symmetry type in the two cases. Hence, in the case of porphin, the transitions are not forbidden by symmetry.

The necessity of adopting a planar oscillator as the model for band II of the neutral porphyrin molecules indicates the presence of two equally-probable transitions, A_{1g}—$\bar{B}_{3u}$ and A_{1g}—$\bar{B}_{2u}$, responsible for this band (the bar over a symbol indicates an electronic-vibrational wave function). An analysis of the direct products for the symmetry groups of D_{2h} shows that such states can arise by excitation of vibrations α_{1g} and β_{1g}. Thus, the electronic spectra of the porphyrins exhibit the totally-symmetric vibration α_{1g}, which does not change the oscillator direction, and the nontotally symmetric vibration β_{1g}, which gives a transition oriented perpendicularly to the 0—0 transition. The equality of the X- and Y-components of the electronic-vibrational bands (formation of a planar oscillator), which is observed experimentally, indicates that these vibrations are manifested equally in the spectrum.

However, as is known, the application of the Franck-Condon principle to complex spectra requires the preferential appearance in the spectrum of the totally-symmetric vibrations. To avoid this contradiction, we must take into account the quasi-forbidden nature of the electronic transitions in the porphyrin molecules.

The group-theoretical discussion given above of the
experimental facts permits us to interpret the ab-
sorption and luminescence spectra of the porphyrins
as follows. Bands I and III in the absorption spec-
trum belong to distinct electronic transitions.
Bands II and IV in the absorption spectrum and band
II in the emission spectrum correspond to electronic
vibrational transitions, with the totally-symmetric
and nontotally-symmetric vibrations manifested to
an equal extent in the spectrum. The diagram of
levels of the porphyrin molecules has the form shown
in Fig. 5. The Soret band corresponds to a sepa-
rate electronic transition."

Next we shall discuss in more detail the work by Platt. Figure 6

shows the spectra of the polyenes as an example of a conjugated chain.

Platt draws attention to the fact that the only organic compounds that

absorb strongly between 2000 and 10,000Å are unsaturated. The strongest

absorbers contain long conjugated chains, ring-chain systems, or sys-

tems of alternating single or double bonds. The spectra are due

principally to excitation of loosely bound, unsaturated electrons or

π-electrons of such systems. In a conjugated pure hydrocarbon, each

carbon atom brings one such electron to the system. These electrons

are largely responsible for the chemical reactivity as well as for the

light absorption of such systems, since they may be excited or removed

from the molecule comparatively easily.

Platt then develops the simplest model possible, namely the free-

electron model.
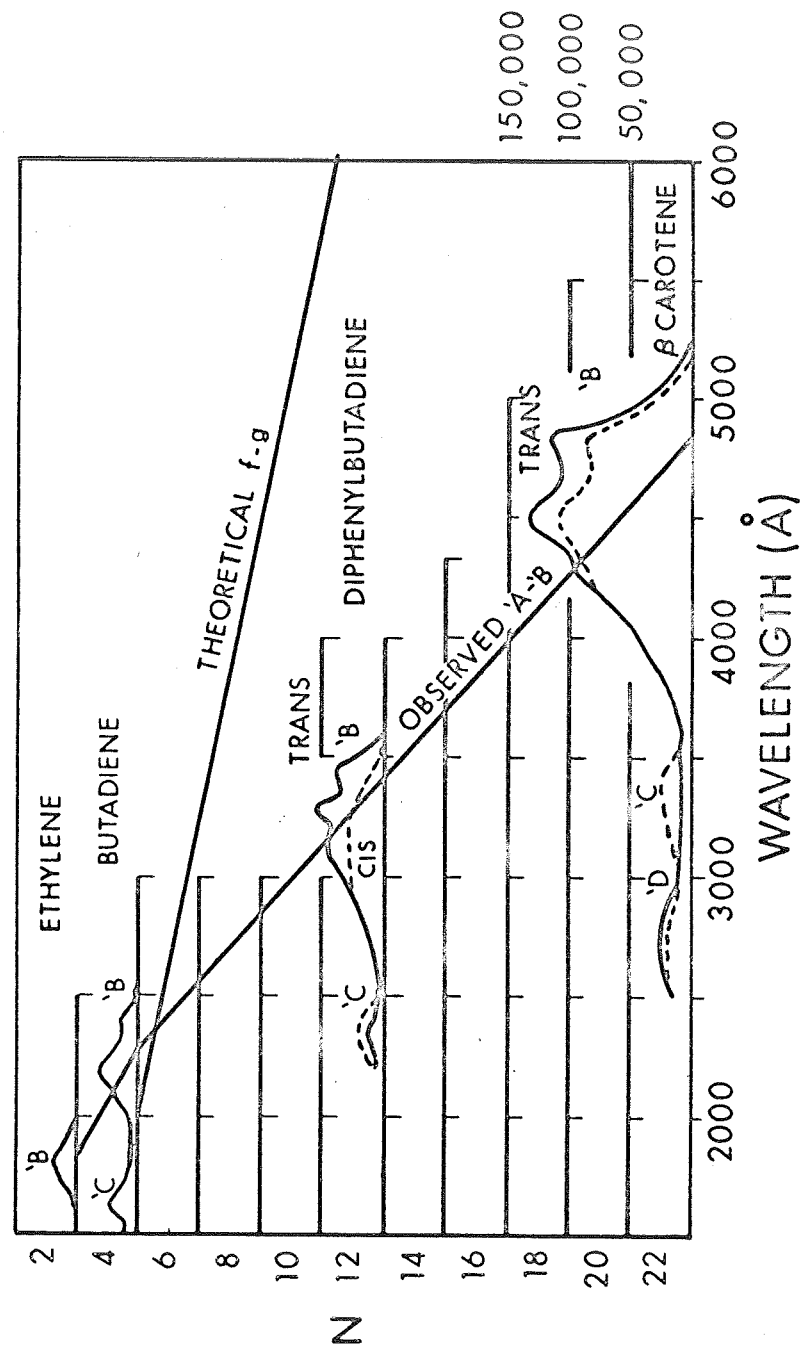
Figure 5. Energy-Level Diagram of the Porphin Molecule
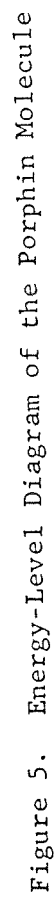
Figure 6. Spectra of Polyenes: Ethylene (Platt et al, 1949), Butadiene (Jacobs and Platt, 1948), Diphenyl Butadiene (Pinckard, et al, 1948), β-carotene (Zechmeister and Polgar, 1943)

THE FREE-ELECTRON MODEL

(from John R. Platt, "Radiation Biology"
Vol. III, A. Hollaender, Editor)

"The main features of the spectra are accounted for
if we assume that the π-electrons are simply con-
fined to a line running the length of the conjugated
system--whether straight or zigzag does not much
matter. If the atomic nuclei are equally spaced
along this line, the potential field in which the
electrons move will look something like the lower
line in Fig. 7, with deep holes near every nu-
cleus. For simplicity, we may approximate this
potential by the one-dimensional "square well"
shown by the straight line, with the potential
constant and equal to zero along the line and ris-
ing to infinity at the ends.

In such a potential well the permissible wave func-
tions ψ are sine functions, vanishing at the ends
of the trough:

$$\psi n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}, \quad n = 1,2,3, \ldots, \qquad (1)$$

where L is the length of the trough and x is the
distance measured from one end. The normaliza-
tion factor that multiplies the sine function is
chosen so that the integral of the electron den-
sity (the square of the wave function) over the
length of the trough,

$$\int_{o}^{L} \psi^2 \, dx,$$

will be unity.

The lowest wave function has a wavelength $\lambda = 2L$,
with no nodes in the trough; the next has $\lambda = 2L/2$,
with one node; the nth has $\lambda = 2L/n$, with n - 1
nodes; and so on, like the oscillations of a vibra-
ting string.

Orbital Energies. The energies of these orbitals are
determined by the de Broglie relation between elec-
tron momentum mv_n and wavelength,
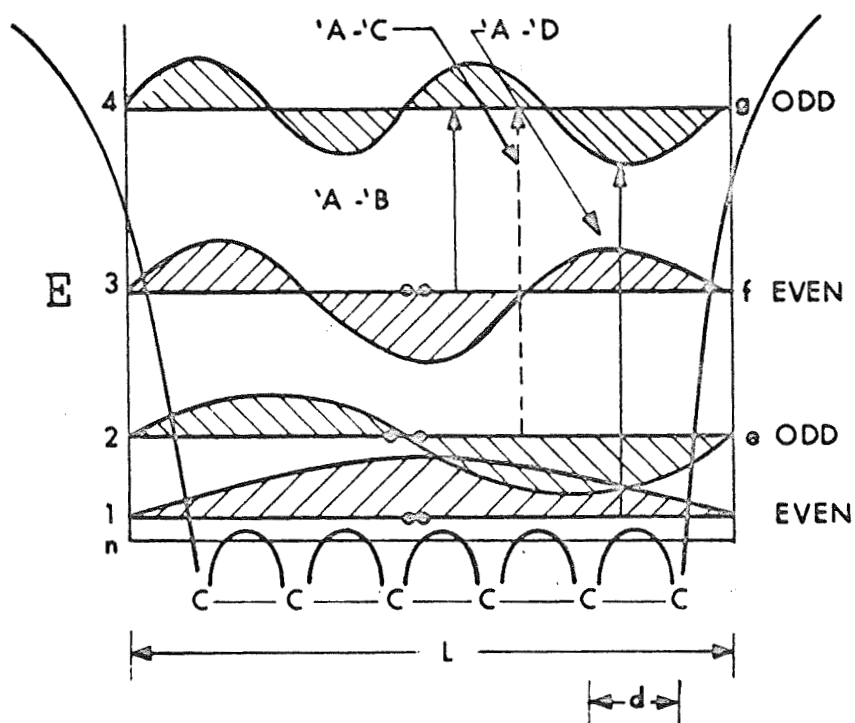
Figure 7. Free-Electron Orbitals, Energies, and Transitions for Hexatriene

73627950

$$mv_n = h/\lambda_n, \tag{2}$$

where m is the electron mass and h is Planck's constant. This relation fixes the electron velocity v_n; and the energy E_n is then

$$E_n = \frac{1}{2} mv_n^2 = \frac{1}{2m} \frac{h^2}{\lambda_n^2} = \frac{n^2 h^2}{8mL^2} \tag{3}$$

The energy varies quadratically with n.

If we assume that the length L for a conjugated chain of N atoms is Nd, where d is the average interatomic distance, then

$$E_n = \frac{n^2 h^2}{8md^2 N^2} = 153,000 \frac{n^2}{N^2} \text{ cm}^{-1}. \tag{4}$$

The second expression gives the energy in wave numbers if d is 1.40 A— the average C—C distance in a conjugated system.

The Pauli principle specifies that only two electrons, of opposite spin, may occupy each orbital. For a polyene where there are N π-electrons in the lowest possible energy state, they then fill up the lowest N/2 orbitals (N is even). The energy required to lift an electron from the highest filled orbital to the lowest unfilled orbital becomes

$$E_{(N/2)+1} - E_{N/2} = \frac{(N/2 + 1)^2 h^2}{8md^2 N^2} - \frac{(N/2)^2 h^2}{8md^2 N^2} \tag{5}$$

or

$$\Delta E = \frac{h^2}{8md^2} \frac{N + 1}{N^2} = 153,000 \frac{N + 1}{N^2} \text{ cm}^{-1}. \tag{6}$$

This should represent approximately the energy of the first spectroscopic transition. For long chains it should vary as 1/N. Note the absence of adjustable parameters. Values predicted by this formula are given by the slanted "theoretical" line in Fig. 6

for comparison with the observed first transitions (marked [1]B). The predicted wavelengths are about right for butadiene. The predictions get poorer with increasing wavelength, varying about twice as fast with N as observed.

The frequency ν of the quantum-mechanical absorption is given by

$$\nu_{Qu} = \Delta E/h. \tag{7}$$

The corresponding classical electromagnetic absorption frequency of a dipole antenna of the same length as the molecule is given by

$$\nu_{Cl} = c/2L, \tag{8}$$

where c is the velocity of light. This frequency is lower than the frequency determined from Eqs. 6 and 7 by a factor h/4mcd, or about 1/230. This simply means that the velocities of the electrons that carry the quantum-mechanical oscillation are smaller by this factor than the electromagnetic-wave velocity, the speed of light. The wavelength absorbed is therefore not 2L, as it would be classically, but about

$$\lambda = 500L. \tag{9}$$

This linear relation between wavelength and molecular length is far from exact in the polyenes, but it helps us understand the approximately constant wavelength shifts introduced by adding additional units to a conjugated chain.

The second absorption frequency of a polyene will be determined by the energy jump that is shown by a dashed line in Fig. 7. This corresponds to the absorption regions marked [1]C in Fig. 6.

Allowed and Forbidden Transitions. The lowest absorption frequency is "allowed," but the second lowest frequency is "forbidden" if the conjugated system is truly a straight line or even if it has a "center of symmetry," as it would have in a polyene in the zigzag trans, trans, . . ., trans form.

These terms have the following significance: For any molecule with a center of symmetry, there are two classes of wave functions, "even" and "odd." Even functions are given by odd values of the integer n in Eqs. 1 to 4. Such a function ψ is exactly equal to itself when reflected in the center of the molecule. The odd functions are given by even n in Eqs. 1 to 4. In them ψ is changed into its negative on reflection in the center; it therefore has a node at the center and vanishes there. (We neglect here the additional node in the plane of the molecule common to all orbitals.)

Now, the "oscillator strength" of a transition can be found experimentally from the integrated absorption intensity,

$$f = 4.32 \times 10^{-9} \int \epsilon_v \, dv, \qquad (10)$$

where ϵ_v is the observed molar extinction as a function of the frequency v in wave numbers. This quantity is predicted theoretically by the expression

$$f = 1.085 \times 10^{-5} v Q^2, \qquad (11)$$

where Q is the "transition matrix element" for one electron to jump from state n to state m:

$$Q_{x,nm} = \int \psi_n x \psi_m \, d\tau \quad (x\text{-component}), \qquad (12)$$

where x is the coordinate measured from the center of the molecule in angstroms and $d\tau$ is the volume element of integration.

The components of Q_{nm} all vanish when both ψ_n and ψ_m are even or when both are odd, and the transition is then "forbidden" (Laporte rule). Actually in a polyatomic molecule there is enough vibrational motion so that the center of symmetry is not preserved. As a result, the transitions that are believed to be of this forbidden type may still be seen, but they are only about one-fifth as strong as their "allowed" counterparts, which are transitions between even and odd orbitals.

Intensities, Polarizations, and Molecular Configu-
rations. On insertion of the free-electron polyene
ψ-functions into the expression for Q, it will be
found that Q is largest for $|n - m| = 1$, i.e., for
the lowest allowed transition, and that the oscil-
lator strength falls off approximately as $1/|n - m|$
for the higher allowed transitions.

For polyenes of different lengths, Q for the first
allowed transition should be proportional to the
length, and f to vQ^2, but since v varies approx-
imately inversely with the length, f is also ap-
proximately proportional to the length. This was
one of the first empirical conclusions from the
comparative study of polyenes (Hausser et al, 1935;
Smakula, 1934). The width of the first polyene ab-
sorption region is approximately constant, and
ϵ_{max} is therefore also approximately proportional
to the length.

Intensity predictions by the LCAO method (Mulliken
and Rieke, 1941) are too large, but their relative
values for different molecules are accurate. Pre-
dictions using the free-electron model appear to
be accurate both absolutely and relatively (Bayliss
1948, 1952; Kuhn, 1948b; Simpson, 1948). The low
allowed transitions of π-electrons in extended
polyenes should be, and apparently are, polarized
along the x-axis; i.e., $Q_y = Q_z = 0$.

If the polyene has one cis link in the middle, so
that it is doubled back on itself like a hairpin,
these intensity relations are changed. The first
transition should become weaker and be polarized
on a line from one tip of the molecule to the other.
The second, instead of being forbidden, may become
stronger than the first and will be polarized along
the axis of the hairpin.

This behavior may be observed in going from the
spectrum of butadiene to that of cyclohexadiene,
where the conjugated system is doubled back on
itself in this way (Mulliken, 1939). It was also
seen in the cis-trans isomerism of longer chains
by Zechmeister and Polgar (1943), Sandoval and
Zechmeister (1947), and Pinckard et al (1948).
These authors called the transition designated as
^1C in Fig. 6 the "cis band" because of its

strength in this molecular configuration. The increase of intensity of a transition in the cis form is then an excellent criterion for the assignment of this transition to the forbidden class in the trans form; the loss of intensity, for its assignment as allowed. Of course, two cis bonds in a molecule, if properly placed, may restore its center of symmetry and make the ^1C transition forbidden again, as Zechmeister found in several cases. It is illuminating to compare his fine classical interpretation of the spectra (1944) with its quantum-mechanical counterpart as given here.

The alternating maxima and minima form a free-electron counterpart to the alternating single and double bonds in the simplest classical valence-bond diagram. Kuhn (1950) gives several examples. The average distance between maxima, or between minima, is just 2d, and the maxima are located in the center of the classical double bonds. The alternation becomes less marked with increasing N and is less marked in the center of the polyene than at the ends. The maxima and minima, from the present point of view, depend on the wave character of electrons, just as do the maxima and minima of different atomic shells in the radial electron densities for an atom. The relation of these polyene density alternations to the classical bond diagrams is then something like the relation between the positions of maximum density in atoms and the Bohr classical orbit radii.

The effect of high electron density at particular points in the polyenes is to attract the neighboring nuclei, producing a shorter bond length and higher force constant. Low density has the opposite effect, so that an alternation of electron densities implies an alternation of bond lengths and force constants. This alternation is well known from the classical valence-bond treatment, as well as experimentally from X-ray diffraction and infrared analysis.

But from the present point of view it could be said that the alternating bond lengths give direct evidence of the wave character of electrons--almost as direct as the Davisson-Germer experiment on the diffraction of electrons from a crystal. The alternation of bond lengths shows the presence of standing waves produced by the internal interference of electron waves reflected from the ends of the molecule.

<u>Effect of Alternation on Transition Frequencies</u>.
Kuhn (1950) has shown how to correct the errors
of the polyene frequency predictions by introduc-
ing an alternation of period 2d into the square-
well potential, as shown in Fig. 8, using deeper
minima near the classical double bonds, where the
nuclei are closer together.

The effect of this periodic perturbation on free-
electron and LCAO orbital energies in molecules,
just as in metals (Seitz, 1940; Brillouin, 1946),
is to enlarge the energy gap between the orbitals
of wavelengths of more than 4d and those of wave-
lengths of less than 4d. In the language of metal
theory, the periodicity introduces a Brillouin
boundary between the first and second Brillouin
zones. But this enlarged gap is just the energy
gap corresponding to the first transition, so that
this transition can now be at higher frequencies
than was predicted by the simple square-well po-
tential, and it fits the observations better.

EMISSION OF LIGHT

The emission of light by an excited molecule is a
process the reverse of the absorption process. It
seems to be controlled, as the absorption is not,
by time-constant considerations. An energy-level
diagram of a typical polyene is shown in Fig. 9.
Between any two states the intensity of emission
is proportional to the intensity of absorption.
By quantum-mechanical laws the time required to
emit a photon is inversely proportional to the in-
tensity of emission and therefore to the intensity
of absorption.

<u>Time Constants</u>. Empirically, for hydrocarbons,
the time constant τ in seconds is given approx-
imately by $10^{-4}/\epsilon_{max}$. Thus, allowed singlet-
singlets, with ϵ_{max} of the order of 100,000, have
a τ of about 10^{-9} sec. Forbidden singlet-singlets,
with ϵ_{max} about 10,000 (in polyenes), have a τ of
about 10^{-8} sec. For a strong singlet-triplet, with
ϵ_{max} about 1, τ will be about 10^{-4} sec. These
emissions are indicated by the solid vertical lines
in Fig. 9.
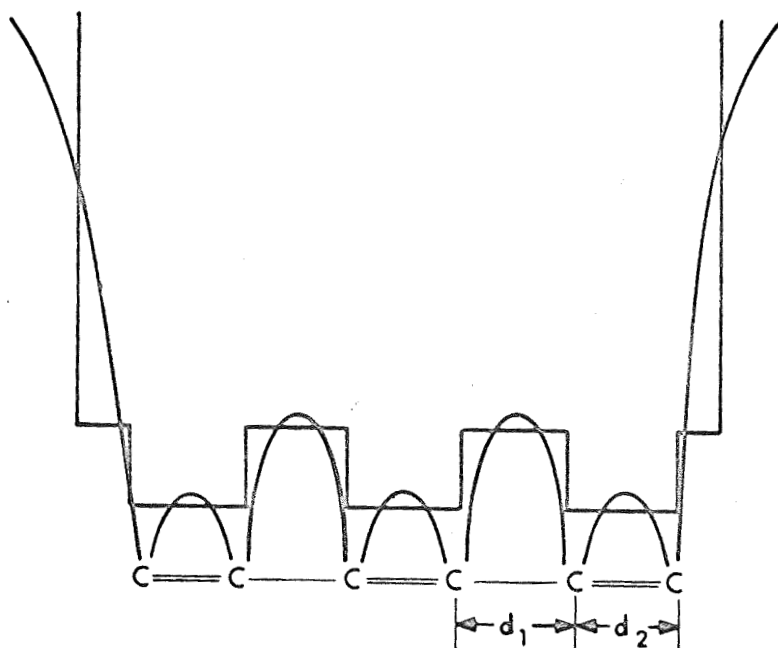
Figure 8.   Free-Electron Potential with Kuhn
Periodicity from Alternating Double
and Single Bonds

73627951

TRIPLETS   SINGLETS

$de^2f^2g \begin{cases} {}^1D^0 \\ {}^3D^0 \end{cases}$ 10^{-7}

10^{-13}

$d^2ef^2g \begin{cases} {}^1C \\ {}^3C \end{cases}$ 10^{-8}

10^{-9} 10^{-13}

10^{-8}

$d^2e^2fg \begin{cases} {}^1B^0 \\ {}^3B^0 \end{cases}$ 10^{-7}

$[10^{-10}]$

10^{-8}

P   F

10^{-4} 10^{-9}

(10^{-5})

$[10^{-7}]$

$d^2e^2f^2A$

GROUND
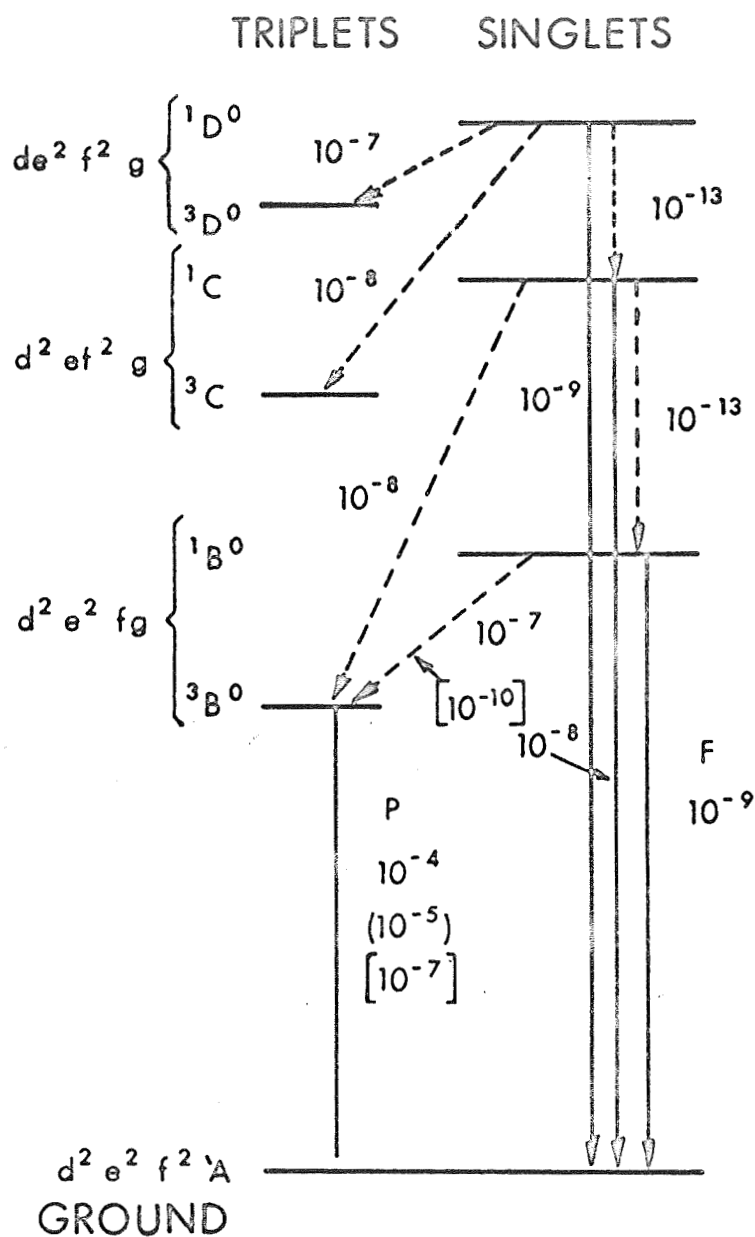
Figure 9. Emission of light by excited organic molecules, lowest
           excited states, B type. Solid lines, radiation; dashed
           lines, radiationless; heaviest lines, most probable route.
           Typical time constants for each type of energy jump are
           given as to order of magnitude, in seconds, for solution
           in viscous light-atom solvents or glasses at low temper-
           ature. Figures in parentheses are possible values under
           thermal quenching at room temperature. Figures in brackets
           are possible values in the presence of heavy atoms, as in
           iodoform solution.

Oscillator strengths are of more theoretical
significance than extinction coefficients. They
are related to the intrinsic time constants as
follows:

$$f\tau = 1.5/v^2 \text{ for fluorescence}$$
$$\approx 2 \times 10^{-9} \text{ sec near 3500 A;}$$

and

$$f\tau = 4.5/v^2 \text{ for phosphorescence}$$
$$\approx 10^{-8} \text{ sec near 5000 A.}$$

But photon emission must compete with other proc-
esses. One such process is radiationless transi-
tion between excited singlets, the result of the
crossing of their potential curves, which we have
not discussed here (Franck and Sponer, 1948). Such
transitions are indicated by dashed lines in Fig.
9. In these a vibrational distortion of the mole-
cule may permit it to go from one excited state by
easy stages into another in times of the order of
a few vibration periods, say, $10^{-12} - 10^{-13}$ sec.
To go from singlet to triplet by this process is
more difficult, since one of the electron spins
must reverse itself at the same time. The time
for this process in a hydrocarbon is more like
10^{-7} sec.

The singlet-singlet radiationless process is much
faster than photon emission or singlet-triplet
radiationless transitions. As a result, the mole-
cule cascades directly down from the higher excited
singlets to the first one in about 10^{-12} sec or less
without light emission. This cascade internally
quenches the fluorescence that might otherwise have
been expected from these higher states.

The first excited state is sufficiently far above
the ground state in most cases so that the radia-
tionless process becomes unimportant. The molecule
may then go from this state to the ground state by
fluorescence (F in Fig. 9) in 10^{-9} sec. Or it may
occasionally go to the lowest triplet in 10^{-7} sec
and from there to the ground state by phosphorescence
(P) in 10^{-4} sec (Lewis and Kasha, 1944).

<u>Energy Transfer</u>. Another type of external quench-
ing which has received much attention lately is the
radiationless transfer of energy from one excited
molecule to another that has a lower-energy excited
configuration (Bowen, 1938; Kallmann and Furst,
1950; Franck and Livingston, 1949; Förster, 1951;
Moodie and Reid, 1952). In mixtures the light
emission may come almost exclusively from the molec-
ular species that has the lowest fluorescent or
phosphorescent state, apparently even when the con-
centration of this species is only a fraction of a
percent, and regardless of what other species has
actually absorbed the light initially.

This "sensitized fluorescence" is a subtle source
of error in luminescence measurements. Correspond-
ingly it may be of great importance in fluorescence
and quenching and in energy transfer between mole-
cules or unconjugated parts of molecules in bio-
logical systems.

PHOTOISOMERISM

Most excited polyene molecules therefore spend a
long time, perhaps 10^{-9} sec, in the first excited
singlet state, and 10^{-5} sec or more in the triplet
state if an appreciable fraction of them get into
this state. These times are long, i.e., by com-
parison with the time needed to execute molecular
vibrations, rearrangement, or dissociation, or
rotations or Brownian motions and collisions lead-
ing to chemical reactions. The excitation energy
is also ample for many chemical effects, 50 kcal/
mole or more for visible absorption, and effects
are easily produced for which the electron density
distribution in the excited state is favorable.

An especially interesting photochemical effect is
the photoisomerization of polyenes, as described
in the classic studies of Zechmeister and Polgar
(1943) on carotenes and in those of Zechmeister
and co-workers on diphenyl butadienes (Sandoval
and Zechmeister, 1947; Pinckard et al., 1948).

RING-CHAIN SYSTEMS

There is a resemblance between polyenes and phenyl chain systems, including phenyl polyenes, diphenyl polyenes, and p-polyphenyls (Platt, 1951a). For every ring in such systems there is one filled orbital v and one empty orbital w of a special type.

The remaining orbitals are independent of these orbitals and are called "polyene type," since they are just the same in number as the orbitals of a simple polyene of the same length, and each orbital resembles closely its polyene counterpart in its symmetry and number of nodes, electron distribution, and energy. In computing the length of the equivalent polyene, each phenyl counts as four atoms. The orbital similarity accounts for the similarity of the long-wavelength spectra of the polyenes to those of phenyl chains, which was one of the earliest important results of spectral comparisons.

Substitution of a vinyl group on the side of a polyene to make a phenyl ring then does not much affect the long-wavelength spectrum of the polyene. Such spectral stability is frequently observed in large conjugated systems, provided the smaller systems that are added are at the side of the large one and not at the end.

Transitions among the polyene orbitals, f-g, e-g, etc., will be polarized approximately along the length of the molecule if it is in the all-trans configuration or is as extended as possible. Transitions between the vinyl orbitals, v-w, $^1A - {}^1H$, etc., will be polarized in approximately the same direction--along the 1,4 axes of the rings.

Transitions between the two groups of orbitals, v-g, $^1A - {}^1G$, etc., will be polarized in the plane of the rings but perpendicular to the 1,4 axes. They will be weak, since the v-orbital is localized, whereas the polyene orbitals are spread out. They will move to the red only about half as fast with increasing chain length as the f-g orbitals. This is the reason that the first transition in benzene and styrene, which is presumed to be of the v-g

type,[*] becomes hidden by the stronger f-g transition in the longer molecules phenyl butadiene and biphenyl. No v-g transitions have been identified in longer ring-chain systems; low-temperature studies are needed.

Some strong absorptions that did not move much with increasing chain length were found in phenyl polyenes by Smakula (1934) near 2000A. These may be the v-w transitions, $^1A-^1H$.

The conclusions reached here about the classification and sequence of transitions in ring chains do not depend on the location of the rings along the chain. Thus the π-electron transitions in quinone are almost identical with those in styrene, which has the same chain length; quinone, of course, has additional weak n-g transitions at long wavelengths, from the oxygen nonbonding electrons.

Analogues of phenyl chains, in which the benzene rings are replaced by thiophene or pyrrole rings, will have similar spectra, except where forbidden transitions in a symmetrical phenyl compound may be enhanced by the loss of symmetry (see Sease and Zechmeister (1947) on polythienyls).

Naphthyl chain systems seem not to have been examined theoretically, but it seems likely that the result will be similar: When the chain becomes longer than the naphthyl group itself, the long-wavelength spectra will begin to have predominantly polyene character.

PORPHYRINS

After the polyenes, the porphyrins open up new vistas of sophistication and interest. These compounds comprise

---

[*]It would not be the first transition except that it is pushed to long wavelengths (and made weak, in benzene) by electron interaction (Platt, 1950, 1951a) between the configurations we are here calling fg and vw (which would be degenerate in benzene). A similar interaction seems to occur in porphin, described later in this chapter.

1. The true porphyrins, which are derivatives of
    porphin (Fig. 10);

2. Chlorins (including rhodins), which are deriva-
    tives of dihydroporphin; and

3. Bacteriochlorins, which are derivatives of
    tetrahydroporphin (Fig. 10) (Rabinowitch, 1944;
    Aronoff, 1950).

PORPHIN

One-electron Orbitals. The orbitals and transition
energies were computed for porphin and tetrahydro-
porphin by Longuet-Higgins et al (1950) using the
LCAO molecular-orbital approximation.[*] The highest
filled and lowest empty orbitals are shown in Fig.
11, and the centers of gravity of the first excited
configurations are shown after them in Fig. 12 for
comparison with the observed excited singlet states.
The orbitals in the columns marked y were computed
assuming the central nitrogen atoms to be equivalent
to carbon atoms. Those marked y' were computed with
a higher electron affinity at the nitrogen positions,
all nitrogen atoms still being assumed equivalent to
each other. The predicted configuration energies
from either set of orbitals fit the observed sing-
let levels about as well as predictions fit in
other molecules when made by the same methods
(Platt, 1950). The symbols at the top of Fig. 11
refer to the symmetry of the wave functions in
standard symmetry notation; in the calculations
porphin was assumed to have D_{4h}, or square, symmetry.

Angular Momentum and Vector Addition. The funda-
mental difference between porphyrins and the poly-
enes stems from the fact that the conjugated system
of porphyrins is not linear but has a two-dimensional
extension in its own plane. As a result, some orbitals
of porphin such as the lowest unfilled one (in the E_g
column of Fig. 11, which we again call the g-orbital,
are doubly degenerate. That is, they consist of two
orbitals, one pointed in the x direction of the square
the other in the y direction, the two components being
of equal energy because these directions are physically
indistinguishable if and when porphin is square.

---

[*]Including consideration of the overlap integral
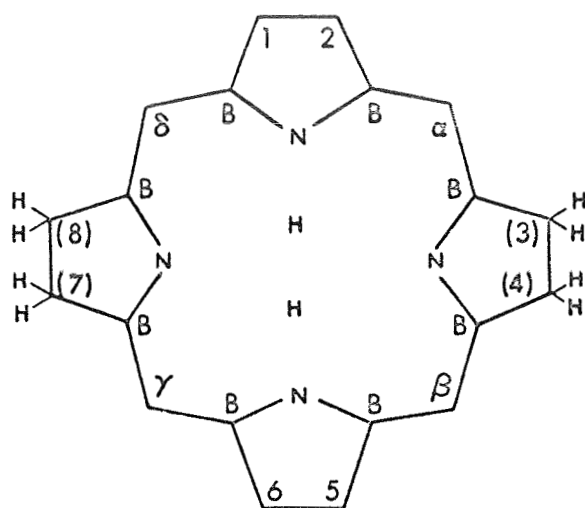
TETRAHYDROPORPHIN
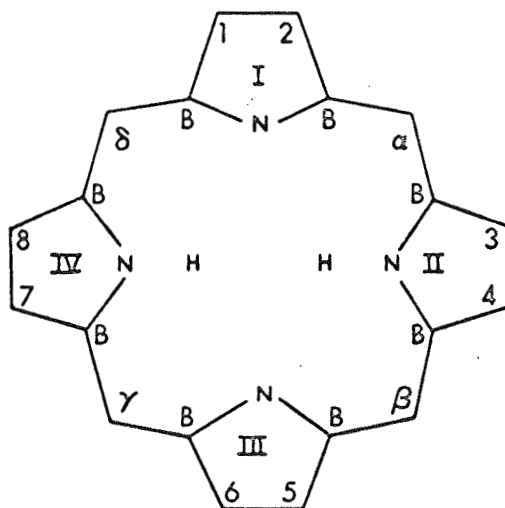
PORPHIN

Figure 10.   Structure and Numbering of Positions of
Porphin and Tetrahydroporphin
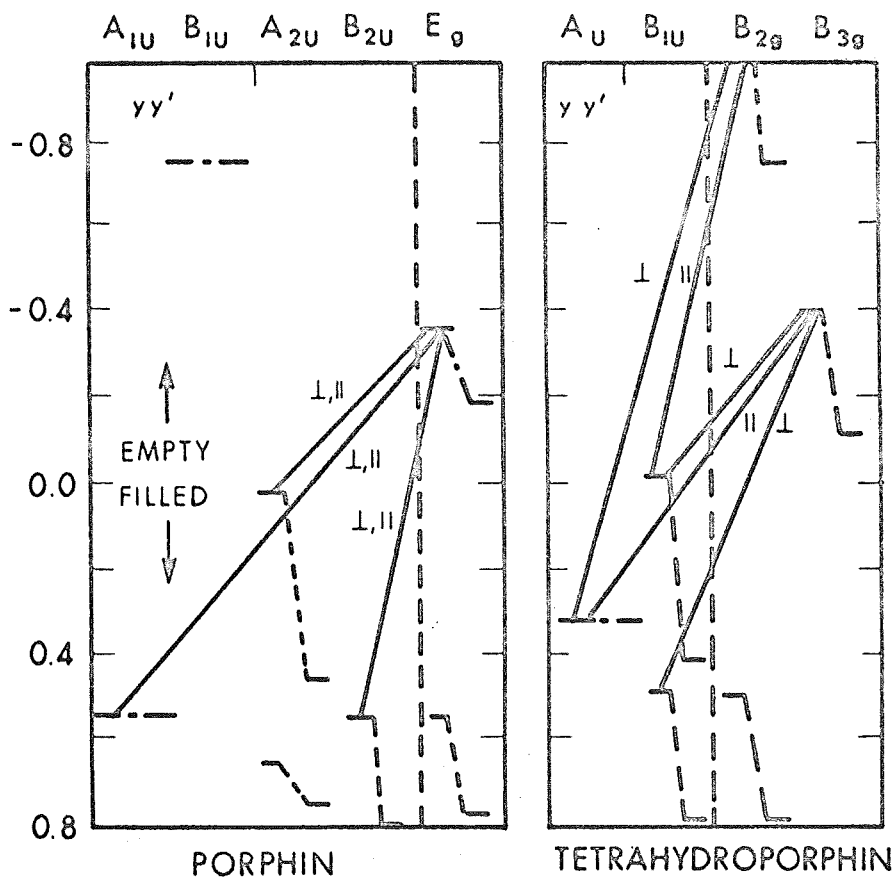
Figure 11. Orbital energies according to symmetry classes, and lowest allowed transitions in porphin and tetrahydroporphin. The double symbol ⊥, ‖ indicates double degeneracy. The single symbols indicate polarization with respect to the longest axis of the conjugated system in tetrahydroporphin
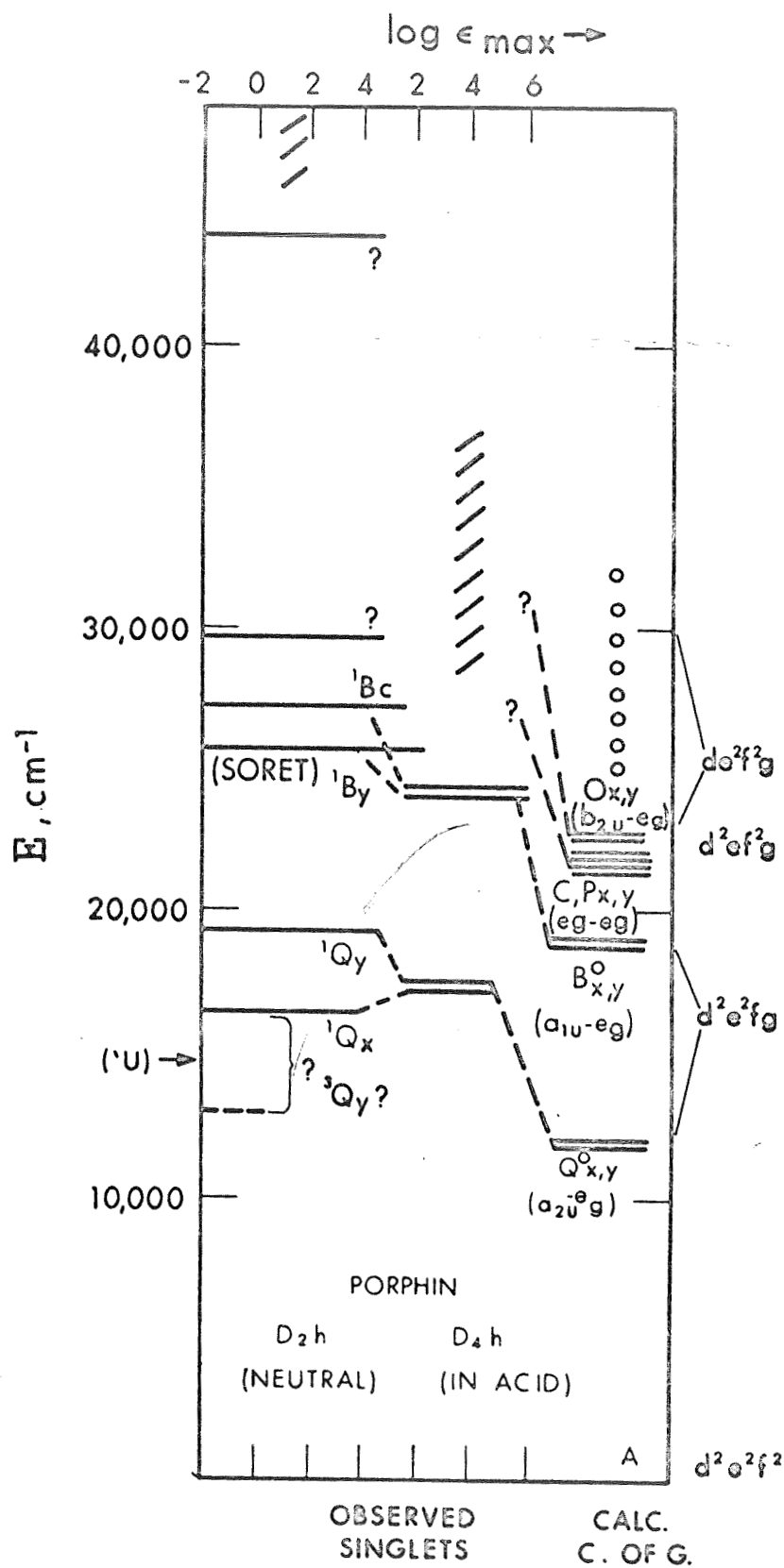
Figure 12. Comparison of Calculated with Observed Energy States for Porphin.

Or we may equally well think of the electron as
switching rapidly from one of these components to
the other and so traveling clockwise (one compo-
nent) or counterclockwise (the other component)
around the ring. This degeneracy in the g-orbital
makes each of the long-wavelength transitions of
porphin also doubly degenerate, with two components
polarized in mutually perpendicular directions
(Fig. 12).

In a two-dimensional conjugated system it also often
happens that other pairs of orbitals that are not
strictly degenerate, like the E_{2g}, are nevertheless
almost degenerate, as, for instance, the highest
filled pair, A_{1u} and A_{2u}, in the y' columns of
porphin. This suggests a modification of the LCAO
results, as follows: To a certain approximation
we may treat such a pair of orbitals in the same
way that we treated the E_g orbital, i.e., as though
they were components of a doubly degenerate f-orbital,
with the electron in one component moving clockwise
around the ring, in the other counterclockwise
(Platt, 1949, 1950).

This combined f-orbital may then be thought of as
having an angular momentum, in this case with a
value of four atomic units; i.e., the A_{1u} and A_{2u}
components out of which we made this orbital are
each crossed through the center by four nodal lines.
They are both odd functions, which change sign on
inversion in the center of symmetry. The g-orbital,
of E_g type, is even and is crossed by five nodal
lines through the center, so that it has an effec-
tive angular momentum of 5 units.

On exciting an electron of angular momentum 4 to
angular momentum 5, the two momenta may be either
in the same direction, and add, or in the opposite
direction, and subtract. The whole molecule, which
began in its ground state ^1A with total angular
momentum 0, may then change its angular momentum
to a value of 1 unit (5 — 4) clockwise or counter-
clockwise, or of 9 units (5 + 4) clockwise or
counterclockwise. These two values of momentum
will give two degenerate singlet states and two
degenerate triplet states for the first excited
configuration, . . . d^2e^2fg. We call these states
$^1B^o$, $^1Q^o$ and $^3B^o$, $^3Q^o$, where B refers to 1 unit of

angular momentum and Q to 9. Electron interaction
will push the B and Q states apart, with the Q lying
lower (Hund rule); triplets of each type will again
lie below singlets of the same type.

The important prediction that this trick of adding
angular-momentum vectors makes possible is that
transitions from the ground state to the low Q
states will be comparatively weak because large
changes of angular momentum are forbidden, where-
as the transition to the higher B states will be
strong and highly allowed. This is precisely the
difference between the porphin absorptions to the
two lowest excited states, as shown in Fig. 12.
In the visible bands of porphin, near 18,000 cm^{-1},
the observed molar extinction ϵ_{max} is about 10,000;
in the violet or "Soret" bands near 24,000 cm^{-1},
it is about 200,000. This is a general result;
comparatively weak long-wavelength transitions in
π-electron spectra are peculiar to molecules ex-
tended in two dimensions, especially symmetrical
ones.

Here the symbol Q has been given to the low state
of high momentum, instead of the symbol L that was
used for the same kind of state in benzene and the
condensed-ring systems (Platt, 1949), because the
properties of the Q state are very different, for
instance, in its behavior with chemical substitu-
tion, as will be seen later.

The prediction of weakness of the first transition
by the vector model is a result not easily obtained
by the usual (one-electron) method, which simply
predicts that the first two transitions of porphin
will be allowed. Configuration interaction must be
considered in such calculations before any substan-
tial difference is found in the predicted intensi-
ties of the first two transitions. Simpson (1949)
first made this prediction of weakness for porphin
by applying vector addition to a free-electron model,
but he oversimplified the problem unnecessarily by
restricting his electrons to a closed 18-atom loop,
leaving out of consideration six other atoms in the
porphin conjugated system. When some of these atoms
are actually missing from the conjugated system, so
that it is more similar to Simpson's model, the first
transition loses its weakness, as will be seen later,
and no longer agrees with Simpson's prediction.

Summarizing, we identify the visible bands of square (D_{4h}) porphin from these theoretical considerations as the $e^2 f^2$ ^1A-$e^2 f g$ $^1Q^o$ transition, degenerate and almost forbidden, and the Soret band near 4000A as the $e^2 f^2$ ^1A-$e^2 f g$ $^1B^o$ transition, degenerate and strongly allowed.

<div align="center">STRUCTURE OF THE VISIBLE BANDS</div>

<u>Configuration of Porphin</u>. In neutral porphin the only parts that must violate the D_{4h} symmetry are the two central hydrogens. Discussion raged for years about whether they were normally on opposite nitrogen atoms or on adjacent nitrogen atoms or served as bridges between the nitrogen atoms; or whether all these species were present in an equilibrium mixture, with rapid transformation from one to the other. This problem was settled by Erdman and Corwin (1946), who showed that replacing one of these protons by a methyl group produced little change in the spectrum. Such a N-methyl group would be expected to be rather tightly bound to a single nitrogen and should not undergo very rapid shifts of position to another nitrogen. Also, in the presence of the bulky methyl group, the remaining proton would probably prefer the opposed position for steric reasons. The adjacent configuration, the bridge configuration, and the rapid-transformation hypothesis are therefore unnecessary in accounting for the spectrum. It suffices to assume that the protons are bound by normal covalent bonds to opposed nitrogen atoms.

There are three ways of modifying porphin so that it can have strict D_{4h} symmetry: (1) we may remove the central hydrogens, as in the disodium salt; (2) we may add two additional hydrogen atoms, as in the dihydrochloride or in concentrated acid solution; or (3) we may replace the central hydrogen atoms by a single central atom, as in the copper or zinc complexes. Any of these changes produces a great simplification in the visible spectrum as seen for the dihydrochloride in Fig. 13, and, except for small wavelength shifts, all three changes produce very similar absorption curves.
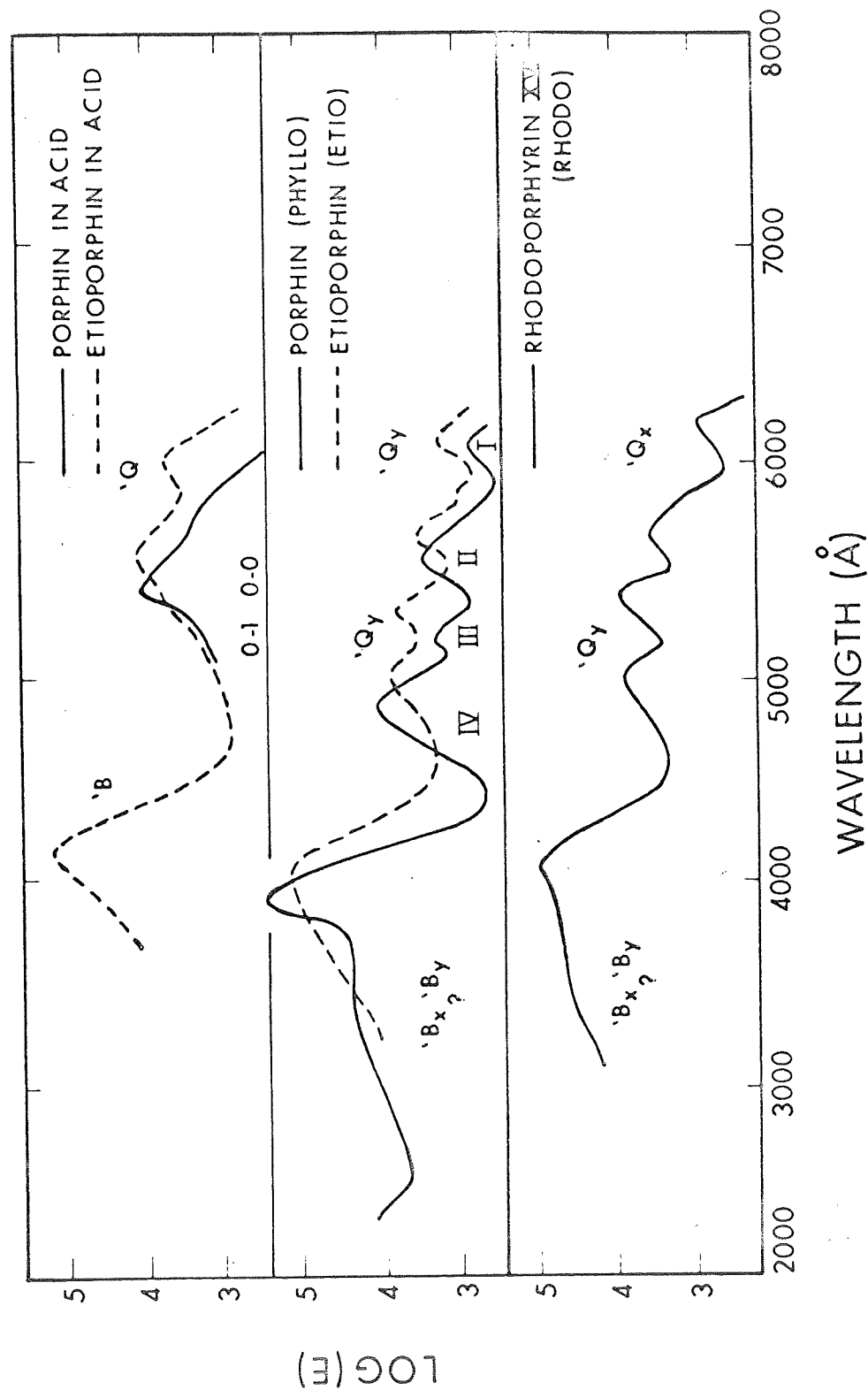
Figure 13. Absorption of Porphyrins (Etioporphyrin from Erdman and Corwin, 1946; others from Stern and Wenderlein, 1935, and Pruckner and Stern, 1936)

Porphin itself in acid has an A-Q transition with only a single sharp peak, and its A-B transition becomes extremely sharp. <u>This</u> must be the spectrum which belongs to the square D_{4h} compound we treated theoretically, with strict degeneracy.

The Interpretation of the Visible Bands. The observed single $^1A-^1Q$ peak in acid can be interpreted as a 0-1 vibrational band, normally the second peak in an absorption-band system. The first, or 0-0 band, is completely absent, as it would be in a strictly forbidden transition, and it appears only when the system is slightly perturbed, as by alkyl substitution. The one observed $^1A-^1B$ peak in acid is presumably the 0-0 band, for it does not acquire a longer-wavelength companion with alkyl substitution.

If this is the D_{4h} spectrum, the complexities of the free-base porphin spectrum are evidently due to the change to D_{2h}, or rectangular, symmetry, with removal of the degeneracy, when two protons only are present in the center. A change of symmetry from external substitution on the ring gives less dramatic spectral changes than when the central symmetry is altered.

The visible spectrum of neutral D_{2h} porphin looks like a superposition of two of the D_{4h} spectra, shifted 800 A apart. This separation is what would be expected when the degeneracy of the upper ^1Q state is removed. It therefore seems reasonable to assign the four visible bands I, II, III, IV (numbered from the red end) as follows:

> Bands I and II: 0-0 and 0-1 vibrations of $^1A-^1Q_x^o$,
>
> Bands III and IV: 0-0 and 0-1 vibrations of $^1A-^1Q_y^o$,

where Q_x and Q_y are polarized in mutually perpendicular directions, whose relations to the H-H axis of the central protons has yet to be determined.

EFFECT OF SUBSTITUTIONS

The effect of substituents on forbidden transitions is easier and more entertaining to compute than the effects on allowed transitions. In the porphyrin visible bands, the intensity changes with substitution are especially interesting. Several "types" of spectra have been distinguished (Stern and Wenderlein, 1936, V; Rabinowitch, 1944) according to the relative intensities of the different band maxima and have been roughly correlated with the presence or absence of certain kinds of substitutions. The spectra are different enough to be used for following reactions, for identification, and for analysis.

Application to Porphyrins. This theory can be adapted to interpret the changes in the visible bands of the porphyrins. The reasoning is as follows:

Substitution in porphins usually seems to strengthen the I and III, or 0-0, bands, of the two electronic components, leaving almost unchanged the II and IV, or 0-1, bands. Therefore the $^1A-^1Q^o$ wave functions are being mixed with the wave function of nearby allowed transitions that have strong 0-0 absorption peaks. Probably these are the $^1A-^1B^o$ transitions. We shall show how the peak intensities can be predicted in bands I and III, which grow from essentially zero values in D_{4h} porphin.

LIGHT EMISSION

Calvin and Dorough (1947) found a weak phosphorescence of chlorophyll b at 8600 A, about 4000 cm^{-1} to the red of its ^1Q_x band and 6800 cm^{-1} from ^1Q_y, with a lifetime of 3×10^{-2} sec. A more definite result was obtained by the same authors (1948) on zinc tetraphenylchlorin, which had a phosphorescence at 8000 A, 3500 cm^{-1} to the red of its ^1Q_x band and 5700 cm^{-1} from ^1Q_y, with a lifetime of about 10^{-2} sec. The triplet upper state of these phosphorescences could be either ^3Q_x or ^3Q_y. The lifetime given is so short that it would surely be related to a strong singlet, were it not for the fact that the heavy zinc atom will shorten the phosphorescence lifetime, as described earlier.

In fact, the difference in the weight of the metal atoms may account for the differences in the intensities and lifetimes of the phosphorescences in these two compounds.

In the C_{18} and C_{22} condensed-ring hydrocarbons, the lowest triplet is always at an almost constant distance of about 9000 cm^{-1} below a "corresponding" singlet (Klevens and Platt, 1949), but whether this correspondence means that both states belong to the same orbital wave function is still being debated. In porphyrins the gap from the triplet to ^1Q_y is more like this figure than the distance to ^1Q_x, so that we may say that ^1Q_y is probably the "corresponding" singlet. Provisionally we may label the triplet as ^3Q_y. However, the separation from ^1Q_x is still within the range of other triplet-singlet separations expected in condensed-ring systems. A determination of the phosphorescent-fluorescent separation in a porphin, a dihydroporphin, and a tetrahydroporphin would settle this question of the "correspondence." If the separation is constant, a correspondence of the triplet with ^1Q_x is indicated; if it gets smaller (by 2000-4000 cm^{1}) in the hydroporphins, then the correspondence is with ^3Q_y.

The changes in fluorescence found by Livingston and coworkers (1949) are more peculiar. They established that strictly dry chlorophyll a or b in a dry solvent probably has no fluorescence, but that minute quantities of "activators" bring the fluorescence up to full strength in both compounds. These activators are polar substances that can form hydrogen bonds, e.g., water, alcohols, acids, or amines. They showed that the activators form a 1-to-1 complex with the chlorophyll and that the complex is the fluorescing agent.

The discussion in this chapter suggests a hypothesis that might account for this fluorescence behavior. It is that there is another electronic singlet state in dry chlorophyll a or b, below but close to the ^1Q_x state, possibly a ^1U_x or ^1W_x state of the carbonyl group in the isocyclic ring of chlorophyll (phorbide type). A molecule the size of chlorophyll, with the π-transitions moved down to 16,000 cm^{-1}, they might just be catching up with the carbonyl n-transitions. A low ^1U or a low ^1W state, with

transitions to ground between 40 and 1000 times
weaker than for ^1Q_x, would be relatively nonfluo-
rescent. (This would be a favorable situation for
finding phosphorescence.) It would not be detected
in absorption on the side of the strong ^1Q_x band
until it was several hundred wave numbers lower
(see Fig. 12); and it would move to the blue in the
presence of polar molecules or protons, as described
earlier in this chapter, perhaps passing above the
^1Q_x and permitting the fluorescence to take place.
Precisely such crossings between low n-transitions
and π-transitions in polar solvents have now been
identified for simpler molecules (McConnell, 1952).

The crossings, if they exist, could be of significance
in biological porphyrins if they served to control the
fluorescent and phosphorescent lifetimes and relative
populations during irradiation.

The possibility that the phosphorescent triplet is
^3U or ^3W seems to be ruled out by the short reported
lifetimes and by the small n-g singlet-triplet sepa-
ration calculated by Reid (1953).

If this explanation is correct, the peculiar fluo-
rescence behavior is not directly related to the
considerable changes in the absorption spectra
which Livingston and coworkers (1949) also found
between the dry and wet chlorophyll. (The shift
in the n-transition would be almost undetectable).
Instead, these spectral changes are simply evidence
of the change in the spectroscopic moment of the
ring substituents when the activator complex is
formed.

For porphyrins capable of forming such complexes,
probably most of the spectra now in the literature
should be ascribed to the complexed molecule, and
spectroscopic moments determined from them should
be attributed to the complex.

REFERENCES

Aronoff, S. (1950) Chem. Revs., 47: 175-195.

Bayliss, N. S. (1948) A "metallic" model for the spectra of conjugated polyenes. J. Chem. Phys., 16: 287-292.

Bayliss, N. S. (1952) The free-electron approximation for conjugated compounds. Quart. Rev. Chem. Soc., 6: 319-339.

Bowen, E. J. (1938) Fluorescence of solids. Nature, 142: 1081.

Brillouin, L. (1946) Wave propagation in periodic structures. McGraw-Hill Book Company, Inc., New York. Pp. 57-65.

Calvin, M. and G. D. Dorough (1947) The phosphorescence of chlorophyll and some chlorin derivatives. Science, 105: 433-434.

Erdman, J. G. and A. H. Corwin (1946) The nature of the N-H bond in the porphyrins. J. Am. Chem. Soc., 68: 1885-1889.

Forster, T. (1947) Zur Deutung der Regelmässigkeiten in den Spektren substituierter Benzole. Z. Naturforsch., A2: 149-153.

Franck, J., and R. Livingston (1949) Remarks on intra- and intermolecular migration of excitation energy. Revs. Mod. Phys., 21: 505-509.

Franck, J. and H. Sponer (1948) Comparison between predissociation and internal conversion in polyatomic molecules. In Contribution à l'étude de la structure moleculaire, Desoer, Liège. Pp. 169-179.

Hausser, K. W., R. Kuhn, and E. Kuhn (1935) Lichtabsorption und Doppelbindung. VI. Über die Fluoreszenz der Diphenylpolyene. Z. physik. Chem., B29: 417-454.

Hausser, K. W., R. Kuhn, and G. Seitz (1935) Lichtabsorption und Doppelbindung. V. Über die Absorption von Verbindungen mit konjugierten Kohlenstoffdoppelbindungen bei tiefer Temperatur. Z. physik. Chem., B29: 391-416.

Hausser, K. W., R. Kuhn, and A. Smakula (1935) Lichtabsorption und Doppelbindung. IV. Diphenylpolyene. Z. physik. Chem., B29: 384-389.

Hausser, K. W., R. Kuhn, A. Smakula, and A. Deutsch (1935) Lichtabsorption und Doppelbindung. III. Untersuchungen in der Furanreihe. Z. physik. Chem., B29: 378-383.

Hausser, K. W., R. Kuhn, A. Smakula, and M. Hoffer (1935) Lichtabsorption und Doppelbindung. II. Polyenaldehyde und Polyencarbonsäuren. Z. physik. Chem., B29: 371-377.

7129-Final

Kallmann, H., and M. Furst (1950) Fluorescence of solutions bombarded with high-energy radiation (energy transport in liquids). Phys. Rev., 79: 857-870.

Klevens, H. B., and J. R. Platt (1949) Spectral resemblances of cata-condensed hydrocarbons. J. Chem. Phys., 17: 470-481.

Kuhn, H. (1948b) Free-electron model for absorption spectra of organic dyes. J. Chem. Phys., 16: 840-841.

Kuhn, H. (1950) Lichtabsorption organischer Farbstoffe. Chimia, 4: 203-218.

Lewis, G. N., and M. Kasha (1944) Phosphorescence and the triplet state. J. Am. Chem. Soc., 66: 2100-2116.

Livingston, R., W. F. Watson, and J. McArdle (1949) Activation of the fluorescence of chlorophyll solutions. J. Am. Chem. Soc., 71: 1542-1550.

Longuet-Higgins, H. C. (1950a) Some studies in molecular orbital theory. I. Resonance structures and molecular orbitals in unsaturated hydrocarbons. J. Chem. Phys., 18: 265-274.

McConnell, II. (1952) Effect of polar solvents on the absorption frequency of $n \rightarrow \pi$ electronic transitions. J. Chem. Phys., 20: 700-703.

Moodie, M. M. and C. Reid (1952) Inter- and intramolecular energy transfer processes. II. Hydrocarbon-hydrocarbon systems. J. Chem. Phys., 20: 1510-1515.

Mulliken, R. S. (1939) Intensities of electronic transitions in molecular spectra. I. Introduction. J. Chem. Phys., 7: 14-20; II. Charge-transfer spectra. Ibid., 20-34; III. Organic molecules with double bonds. Conjugated dienes. Ibid., 121-135; IV. Cyclic dienes and hyperconjugation. Ibid., 339-352; V. Benzene. Ibid., 353-356; VI. Molecular refractivities of organic compounds. Ibid., 356-363; VII. Conjugated polyenes and carotenoids. Ibid., 364-373; VIIIa. Odd-numbered conjugated polyene chain molecules and organic dyes with notes on optical anisotropy and Raman intensities. Ibid., 570-572.

Mulliken, R. S., and C. A. Rieke (1941) Molecular electronic spectra, dispersion, and polarization; the theoretical interpretation and computation of oscillator strengths and intensities. Repts. Progr. Phys., 8: 231-273.

Pinckard, J. H., B. Wille, and L. Zechmeister (1948) A comparative study of the three stereoisomeric 1,4-diphenylbutadienes J. Am. Chem. Soc., 70: 1938-1944.

Platt, J. R. (1949) Classification of spectra of cata-condensed hydrocarbons. J. Chem. Phys., 17: 484-495.

Platt, J. R. (1950) Molecular orbital predictions of organic spectra. J. Chem. Phys., 18: 1168-1173.

Platt, J. R. (1951a) Isoconjugate spectra and variconjugate sequences. J. Chem. Phys., 19: 101-118.

Rabinowitch, E. (1944) Spectra of porphyrins and chlorophyll. Revs. Mod. Phys., 16: 226-235.

Reid, C. (1953) n-π Emission spectra. J. Chem. Phys., 21: 1906.

Sandoval, A., and L. Zechmeister (1947) Some spectroscopic changes connected with the stereoisomerization of diphenylbutadiene. J. Am. Chem. Soc., 69: 553-557.

Sease, J. W., and L. Zechmeister (1947) Chromatographic and spectral characteristics of some polythienyls. J. Am. Chem. Soc., 69: 270.

Seitz, F. (1940) The modern theory of solids. McGraw-Hill Book Company, Inc., New York. Pp. 271-328.

Simpson, W. T. (1948) Electronic states of organic molecules. J. Chem. Phys., 16: 1124-1136.

Simpson, W. T. (1949) On the theory of the π-electron system in porphines. J. Chem. Phys., 17: 1218-1221.

Smakula, A. (1934) Über physikalische Methoden im chemischen Laboratorium. XXII. Lichtabsorption und chemische Konstitution. Z. angew. Chem., 47: 657-665.

Stern, A., and H. Wenderlein (1934) Über die Lichtabsorption der Porphyrine. I. Z. physik. Chem., A170: 337-350.

Stern, A., and H. Wenderlein (1936) Über die Lichtabsorption der Porphyrine. V. Z. physik. Chem., A176: 81-124; VII. Ibid., A177: 165-192.

Zechmeister, L., and A. Polgar (1943) Cis-trans Isomerization and stereochemistry of carotenoids and diphenylpolyenes. Chem. Revs., 34: 267-344.

3.1 PORPHYRINS

In this section we describe some typical spectra taken from the litera-
ture in order to exhibit various effects associated with porphyrin-
type spectra. The inclusion in this report of this data does not
necessarily imply that these compounds constitute interstellar dust
particles. It merely illustrates some of the variations that are
possible and the diverse effects that can be observed. Figure 14
illustrates the temperature effect on the emission spectra of Chlor-
ella at very low temperatures. Note that the emission line at 689 m_μ
peaks sharply as one approaches $4^\circ K$. Figure 15 shows the polarization
spectra of protoporphyrin. In the same graph both the absorption
spectra and luminescence are shown. Figure 16 shows the polarization
spectra of pheophytin as well as the absorption spectra and its com-
pound. Figure 17 shows the absorption spectra of tetraphenylporphine
in toluene. This compound exhibits a rather sharp and strong peak in
the neighborhood of the 4430 line. This data, taken by Linschitz,
also exhibits two types of absorption, the singlet and the triplet,
whose absorption peaks differ — as can be seen on the figure; in fact
it would appear as if the triplet absorption is closer to the 4430
line than the singlet, although the singlet is considerably stronger.
Another example, Fig. 18, taken from a paper by Sauer et al[*], exhibits
another type of phenomena, namely the effect of dimerization. Note
that the monomer has slightly different absorption than the dimer.
This effect can be seen more dramatically by examining the difference
spectrum below the curve. Figure 19, taken from Falk, shows the spectra
of an iron protoporphyrin chelate. Note particularly the relatively
sharp absorption band shown here for pyridine haemochrome.

---

[*] K.Sauer et al, J. Am. Chem. Soc. **88**, 2681 (1966)
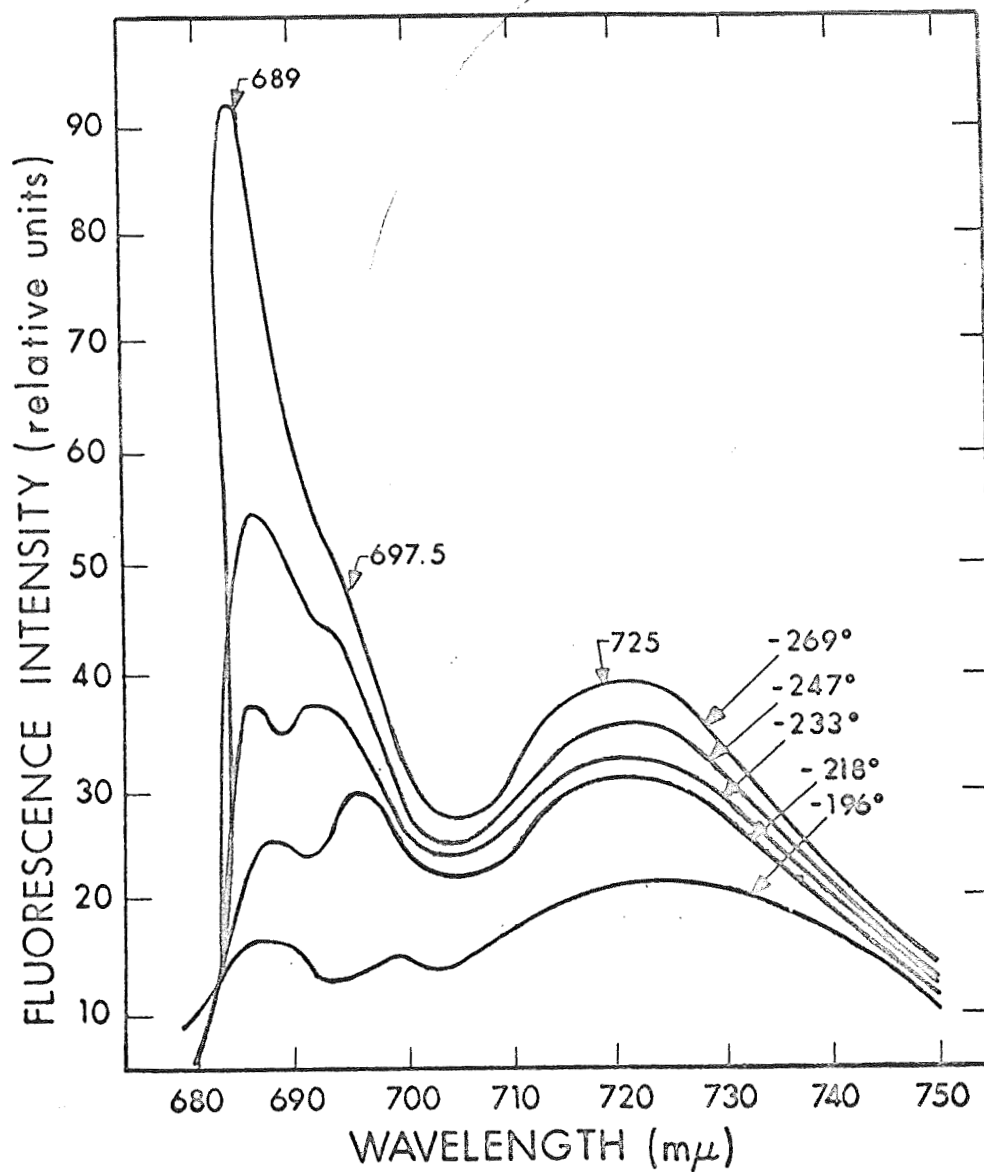
Figure 14.   Emission Spectra of Chlorella Pyrenoidosa as a
Function of Temperature
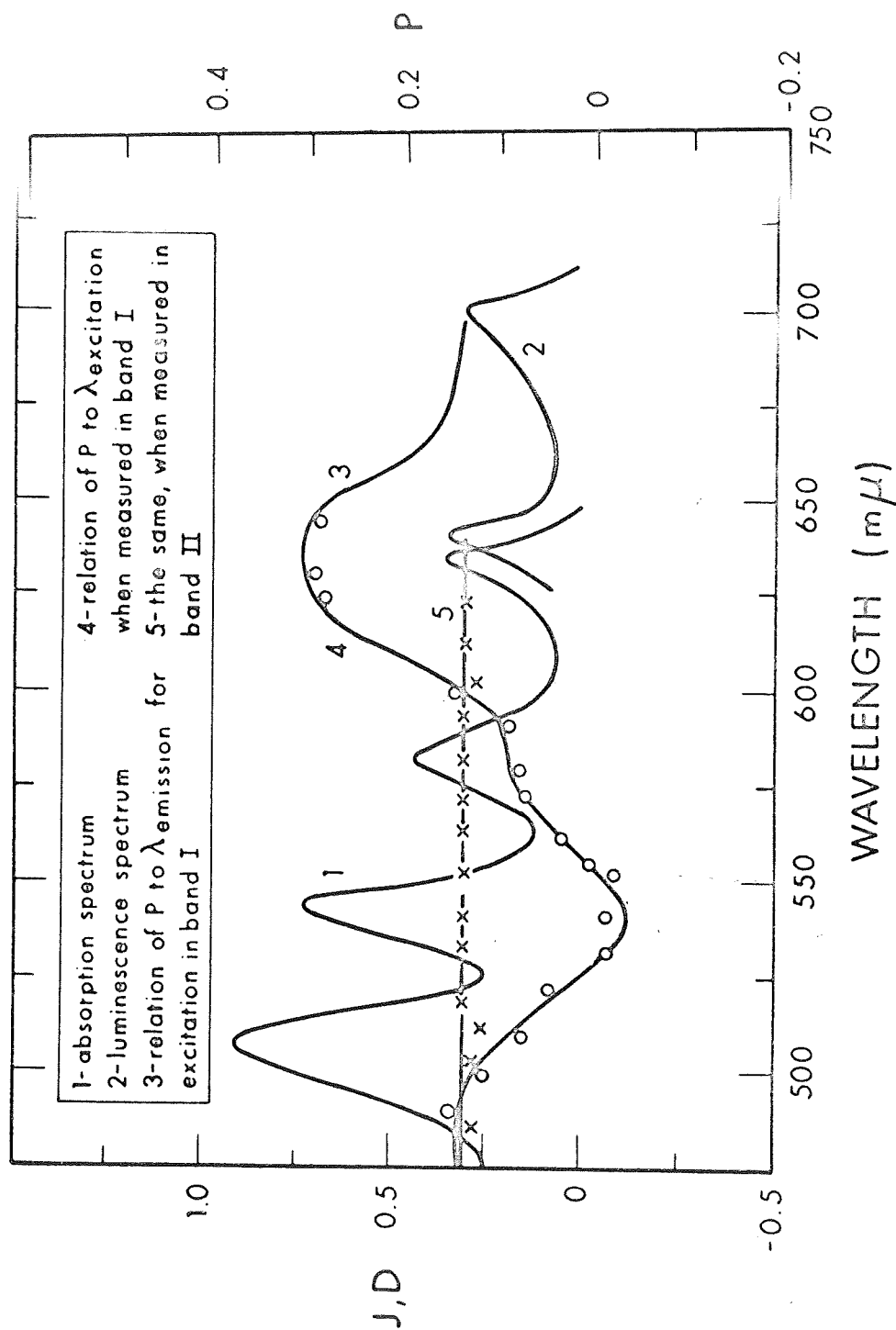
Figure 15. Polarization Spectra of Protoporphyrin
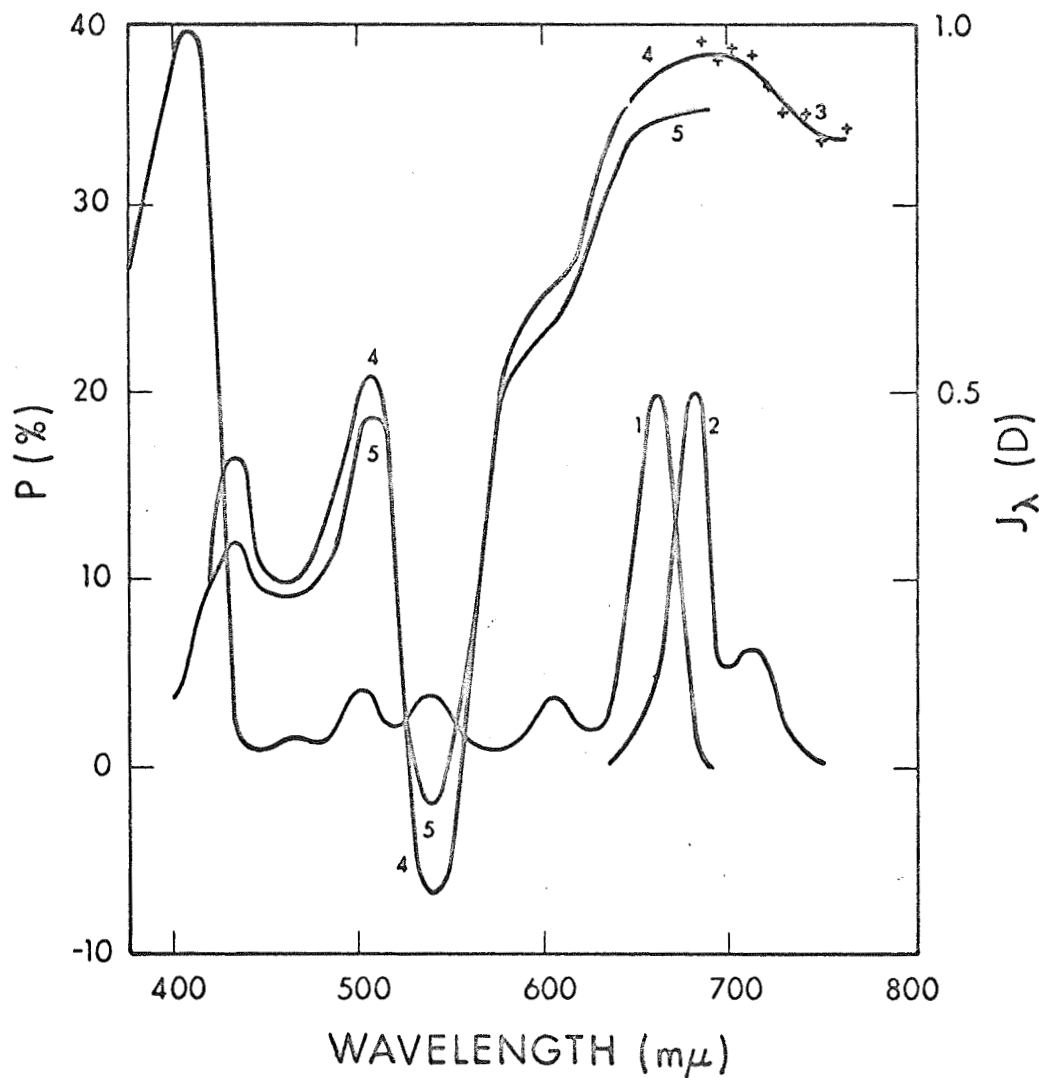
Figure 16.   Polarization Spectra of Pheophytin

7945
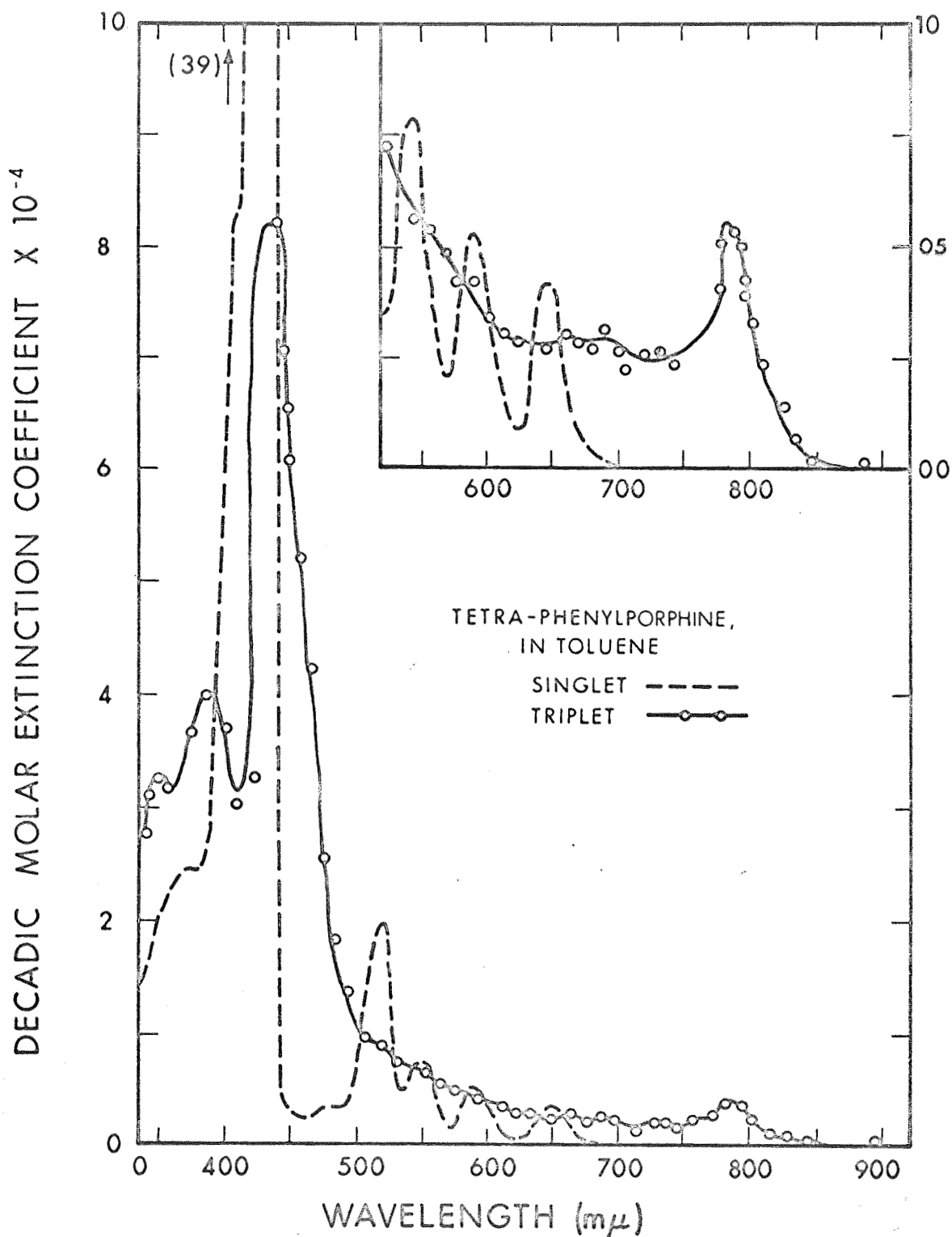
Figure 17.   Absorption Spectra of Tetraphenylporphine and its Triplet
State Corrected to 100% Conversion, in Toluene

73627948
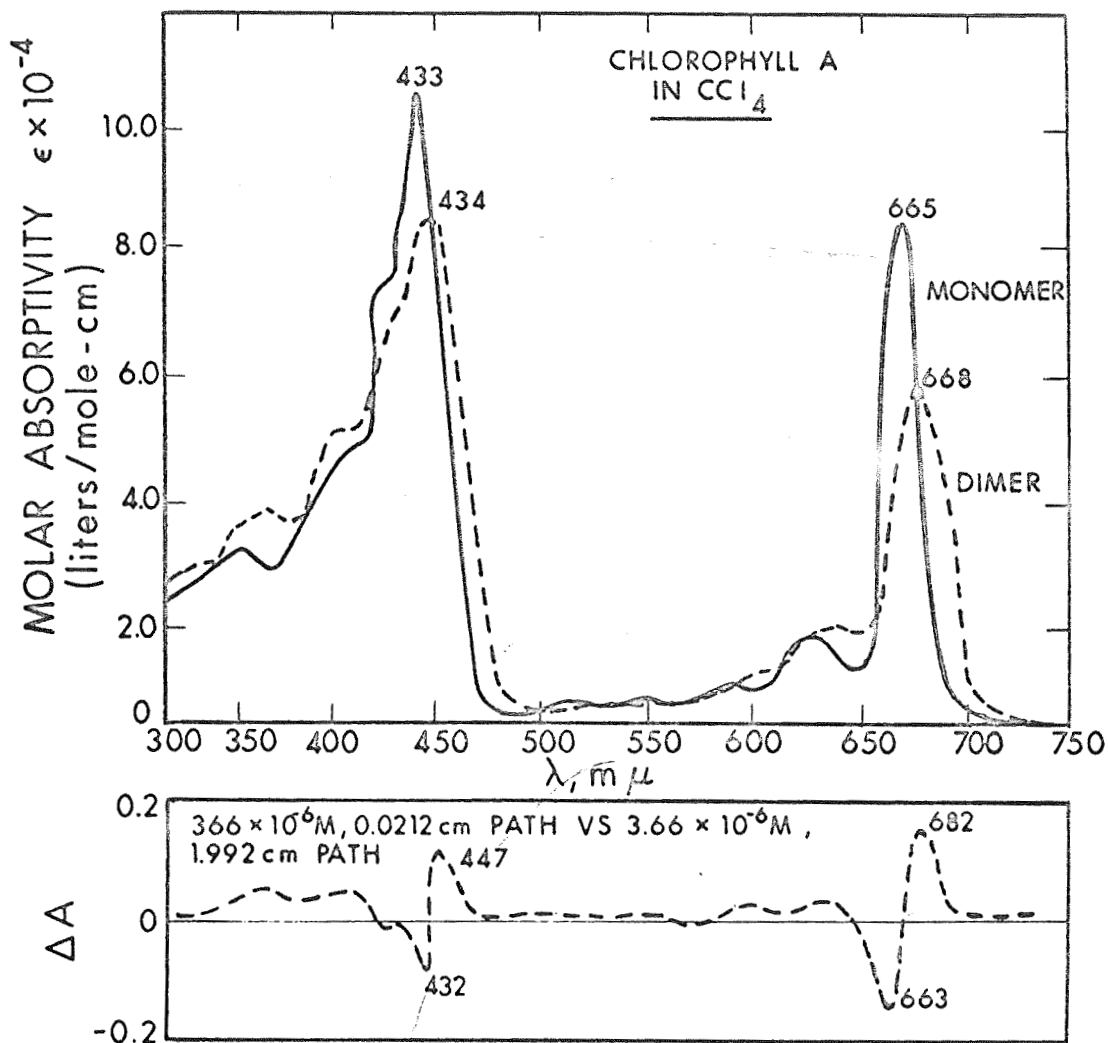
Figure 18. Absorption spectra of chlorophyll a in carbon tetrachloride (upper curves) calculated for pure monomer (solid curves) and pure dimer (dashed curve). Absorptivities are given per mole of monomer in the dimer. The lower curve (dashed) shows a difference spectrum measured directly between two solutions at different concentrations and for path lengths inversely proportional to the concentrations.
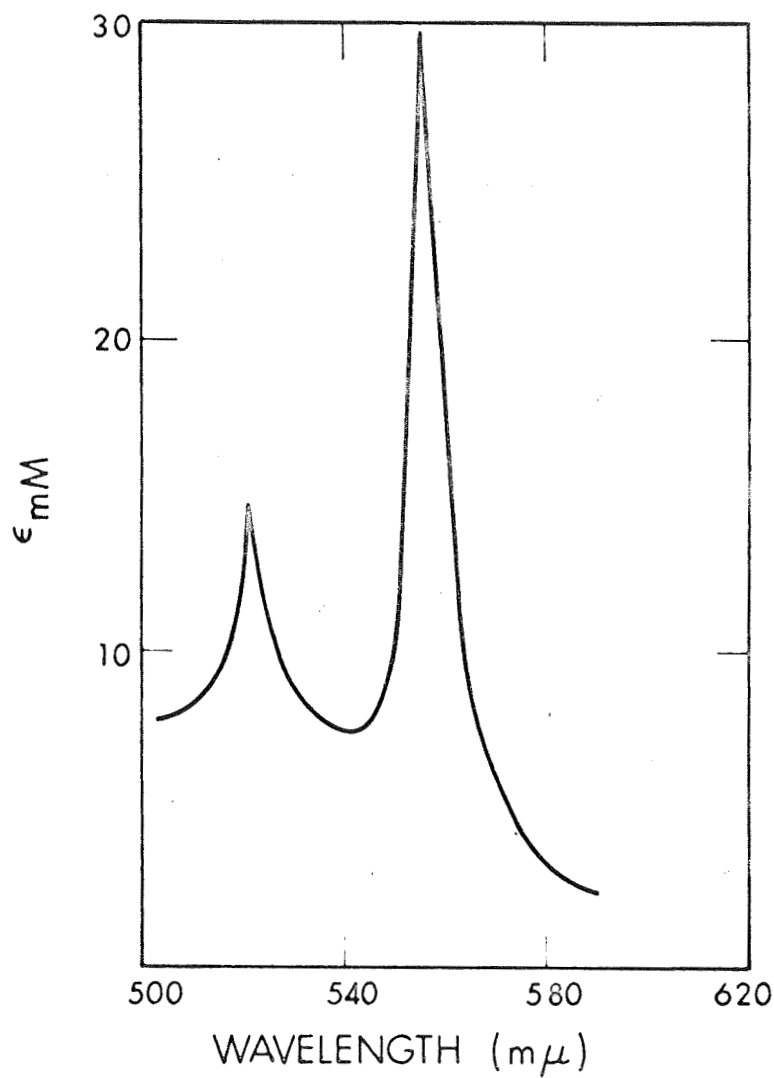
Figure 19. Spectra of Perpendicular Complexes of Iron-
Protoporphyrin Chelates; Pyridine Haemochrome
(Bispyridine-Fe(II)-Porphyrin)

3.2 HAEMATIN COMPOUNDS

Although a great deal of work has been done on the chlorophyll compounds, largely because of their ready accessibility, the haematin compounds deserve more attention, not only because their absorption bands are closely related to the interstellar diffuse lines, but they have other desirable properties such as paramagnetism. Tables II and III reproduced in this report show some of the spectral data obtained by Clezy and Morell.* (Those haemin compounds whose spectra most closely match the diffuse interstellar lines both in intensity as well as wavelength position are underlined in the table.)

It should also be pointed out that the haem compounds show the narrowest absorption lines, as shown particularly by Estabrook,** who took measurements of some of the compounds at lower temperatures. As far as could be determined, no absorption measurements of these compounds had been taken at $4^{\circ}K$.

The relationships between chlorophyll and haems and their synthesis in biosynthetic chain is discussed by S. Granick.[+] Figure 20 shows the biosynthesis from glycine and succinyl-CoA to protoporphyrin, a function of mitochondria and of proplastids. Figure 21 shows hypothesis under control of protoporphyrin biosynthesis and some animal mitochondria. For more details, the reader is referred to the original papers. However, these figures are included to show the importance of these compounds for biosynthesis and for possible exobiological applications.

---

*P. S. Clezy and D. B. Morell, Biochem. Biophys. Acta 71, 165 (1963)
**R. W. Estabrook, "Cytochromes Cooled in Liquid Nitrogen," Haematin Enzymes, Edited by Falk, Lemberg and Morton, Part 2, Pergamon Press (1961)
[+]Vol. 6, Mechanism of Photosynthesis, edited by Tamiya, 1963 Pergamon Press

TABLE II

SPECTRAL DATA OF PYRIDINE HAEMOCHROMES

Corresponding haematin dimethyl ester	Pyridine haemochromes* Absorption ($m\mu$)				
	Found			Literature	
	Soret band	β-band	α-band	β-band	α-band
2,4-Diacetyldeutero-haematin	439	540	573	539.7	575.2
2,4-Diformyldeutero-haematin	450	548-9	584	549.7	584.3
2,4-Diethyldeutero-haematin (meso haematin)	412-3	518	547	518	547
Deuterohaematin**	407	515	545	513.3	544.9
2,4-Divinyldeutero-haematin (protohaematin)	420	525	556	525	558
2-Formyl-4-vinyldeutero-haematin (chlorocruorohaematin)	434	532-4	580.5	545.1	583.1
M-moacetyldeutero-haematin***	422-3	526	570	530	571
p-Formyldeuterohaematin	428	530	578-9	548	578
Haematin a+	427	None	585	None	587
Oxorhodoporphyrin 2-acetyl-6-(des-propionic acid) carboxylic deutero-porphyrin				None	582

*The pyridine haemochromes were prepared in pyridine-0.01 N NaOH + $Na_2S_2O_4$ (I:I, v/v).

**1,3,5,8-Tetramethyl-6,7-di-proprionic acid porphin-Fe^{3+} complex.

***A mixture of the 2- and 4-isomers.

+Substituents on the 2-, 4- and 8-positions are hydroxyalkyl, extended vinyl and formyl, respectively. Other positions are substituted as for deuterohaematin.

58

TABLE III

ABSORPTION MAXIMA OF HAEMIN CHLORIDES AND ALKALINE HAEMATINS

Haemin	Haemin Chlorides Absorption Maxima (mμ)							Alkaline Haematins Maxima (mμ)		
	S'	S	IV	III	II	I	S/S'	S	II	I
2,4-Diformyl deuterohaemin	360	425	517	550	590	645	1.51	425	587	630
Haemin α*	370/80	416	505	550	600	660	1.26	410	573	621
2-Formyl-4-vinyl deuterohaemin (chlorocruorohaemin)	370/80	415	510	548	605/10	650	1.24	406	577	620
4-Formyldeuterohaemin	365/70	411	507	547	600	650	1.32	404	573	616
2,4-Diacetyldeuterohaemin	360/65	417	515	544	590	640	1.54	411	580	605/10
2 + 4-Monoacetyldeuterohaemin	365/75	406	507	540	585	633	1.29	401	574	610
2,4-Divinyldeuterohaemin (protohaemin)	381/2	407	512	539/40	585	638	0.97	399	570	595/600
2,4-Diethyldeuterohaemin (mesohaemin)	370	397	506/8	534	585	632/4	0.84	392	564	590
Deuterohaemin	370	399	505	530	570	626/8	0.96	391	560	585

*Substituents affecting spectrum are 4-vinyl (extended) and 8-formyl
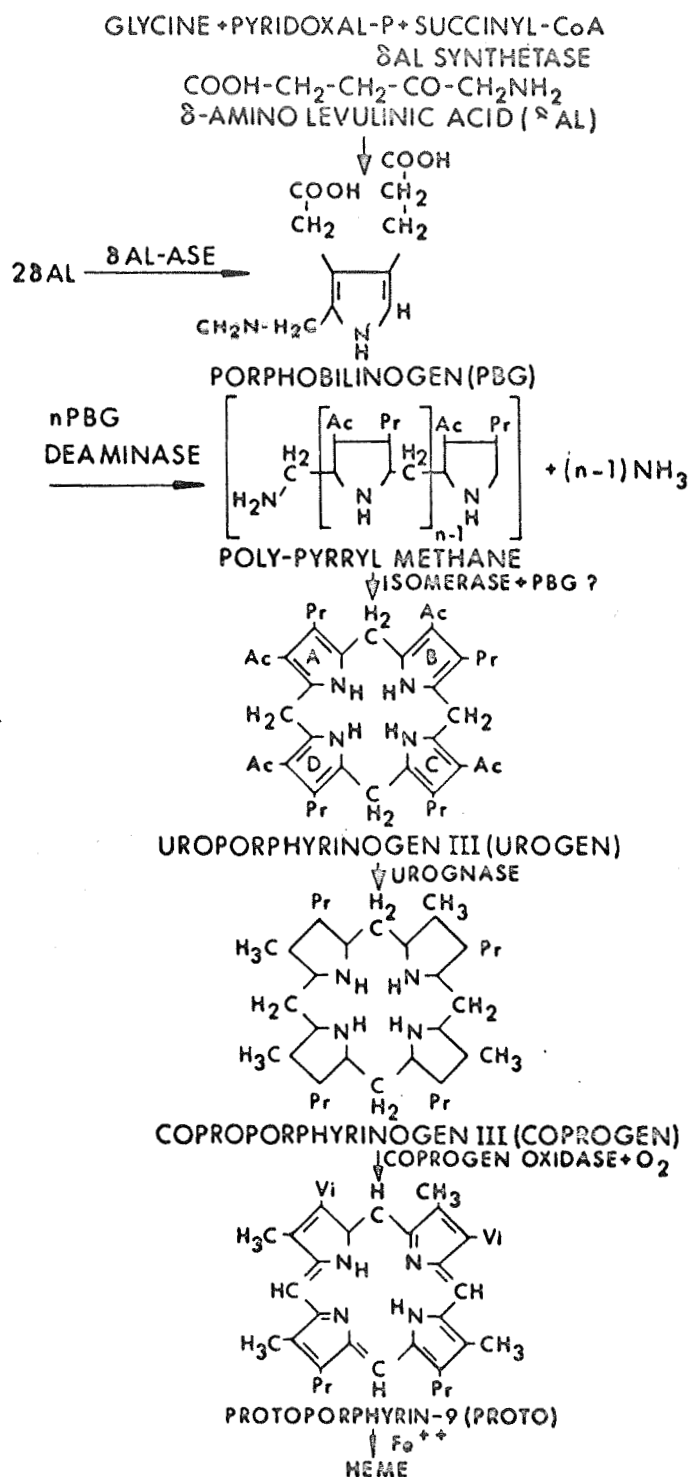
Figure 20. Biosynthesis from Glycine and Succinyl - CoA
to Protoporphyrin, a Function of Mitochondria
and of Proplastids (after Granick)

7129-Final   59

73627970
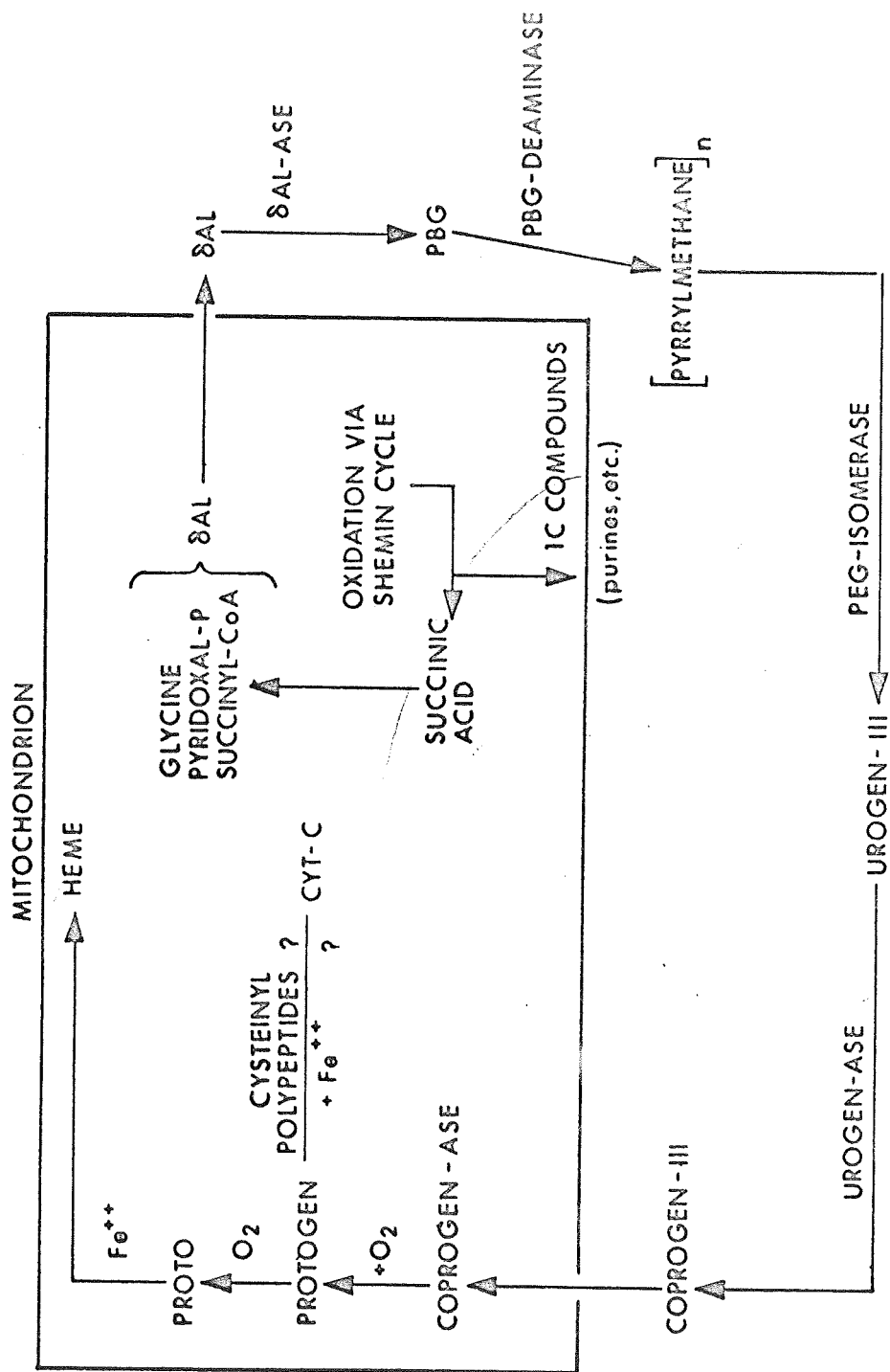
Figure 21. Hypothesis on the Control of Protoporphyrin Biosynthesis in Some Animal Mitochondria by Regulation of the Permeability of the Mitochondrial Membrane (active or passive?) to δ-amino levulinic acid (after Granick)

3627971

A paper by Granick and Mauzerall summarizes the biosynthetic chain for both heme(a) and chlorophyll(b). The general similarity between the two compounds and their biosynthesis is noteworthy. Because of the overall similar structure it is not surprising that their spectra are somewhat similar. Getting back to the spectra of the haem compounds: the visible spectra of the haems are largely those of the porphyrin ring. The rather small shift observed between most metals (about 500Å) agrees with the limited interaction between the localized metal cation orbitals and the π-electrons of the porphyrin ring, the latter (including the unshared pairs on the nitrogens) being responsible for the visible spectra.

Ferrous haems show two strong bands between 5000 and 6000Å. The ferric ion causes a general weakening of the visible spectrum, the lines being broader. Moreover the absorption extends to longer wavelengths. The band in the region of 6300Å is thought to be due to a charge transfer from the ligand to the ferric ion. Note the strong interstellar diffused absorption band at 6284Å, which might correspond to this charge transfer band. The haem complexes also have weaker bands, whose intensity is less than 1/100 of the Soret band in the region 7000 to 15,000Å. Although for a series of methemoglobin compound complexes, intensities comparable to the visible band for high-spin complexes exist.

Since there is a close chemical relationship between the haems and cytochromes, it is not surprising that the absorption bands for either the haem or the cytochrome are similar. For discussion of the cytochromes, see article by Green and Fleicher.[*] The cytochromes play an important role in the electron transfer system and in mitochondria.

_____

[*]"Metabolic Pathways," edited by D. M. Greenberg, 1960 Academic Press, p. 62

The monomeric form of cytochrome a contains two molecules of copper
and one molecule of haem per 72,000 grams. The molecular weight of
cytochrome b is about 20,000. The spectra of cytochrome a show two
typical bands, one at 6050Å and the other Soret band at 4440Å. See the
work by Morell et al, described in Haematin Enzymes.* Tables IV and
V, of this paper list the absorption spectra for ferric and ferrous
heme compounds as a function of pH and associated compounds. The ferric
compound characteristically shows the haematin band associated with the
charge transfer band and possibly corresponding to the diffuse inter-
stellar line 6284. The Soret band around 4000Å does not correspond
with 4428; however, two broad absorption peaks discovered by Herbig
and tentatively identified by him as belonging to the diffuse inter-
stellar lines would clarify this problem. Furthermore, the visible
absorption bands at 5451 and 5778, as well as 6176Å should not be
neglected in the comparison, since the ferric haem has bands centered
around the region 5870Å to 5900Å, which would possibly correspond with
the interstellar 5778, and the ferrous haem has characteristically
weaker bands corresponding to the 5451Å interstellar line. Again it
must be cautioned that although this data is very suggestive, the ab-
sorption measurements were taken in solutions and not in the appropriate
small grain structure cooled to $4^{o}K$. (It is planned to repeat these
measurements in the follow-on program, particularly in Task B, since
it is necessary to purify and synthesize some of these haem compounds.)

---

*IUB Symposium Series, Vol. 19, edited by Falk, Lemberg and Morten,
Part I, Pergamon Press, 1961

TABLE IV

FERRIC HAEMATIN a COMPOUNDS

λ in mμ, in parentheses approximate ϵ_{mM}

Compound of haematin a with	pH	Buffer	Alkaline	Ferri haemo-chrome band	Weak bands	Soret band
OH—	13	0.1 N NaOH	635(9.5)	—	none	405(59)
	9.0	0.05 M borate	630(8.9)	—	none	400(61)
	7.5	0.05 M barbital	635(7.9)	—	none	400(67)
CN— (0.1 M)	13	0.1 N NaOH	635(9.0)	—	none	405(60)
Pyridine (20%	13	0.1 N NaOH	635(7.9)	587(7.5)	none	418(64)
	9.0	0.05 M borate	635(7.2)	587(7.8)	to 530	410(81)
		water	—	587(12.0)	540(10.9)	414(111)
4-Methylimidazole (2%)	9.0	0.05 M borate	—	597(14.1)	548(12.0)	434(66)
Native human globin (1%)	9.0	0.05 M borate	635(6.9)	590(8.6)	none	418(77)
		0.2 M Na$_2$HPO$_4$	635(8.0)	590(11.7)	none	410(71)
HRP-apoperoxidase (0.5%)	9.0	0.05 M borate	640(8.5)	585(7.3)	none	405(50)
Human serum albumin (0.5%)	9.0	0.05 M borate	635(7.9)	590(8.8)	none	410(79)
	7.5	0.05 M barbital	630(8.8)	590(9.7)	none	405(45)
Ox serum albumin (cryst)(0.5%)	7.5	0.05 M barbital	635(8.8)	590(9.7)	none	405(40)
Alkali-denatured human globin (0.5%)	13	0.1 N NaOH	635(6.6)	585(5.8)	none	414(41)
Alkali-denatured ox serum globin (0.5%)	13	0.1 N NaOH	630(8.4)	587(9.6)	none	407(78)

TABLE V

FERROUS HAEM α COMPOUNDS

λ in mμ, in parentheses ε_{mM}. Reductant: dithionite

Compound of Haem α with	pH	Buffer	α-band	Weak bands	Soret (γ) band	Ratio γ/α
Water	9	0·05 M borate	600-605(11·1)	none	415(56)	5·0
	7·5	0:05 M barbital	598(9·7)	none	410(69)	6·9
CO	9	0·05 M borate	602·5(24·7)	none	425(105)	5·0
	7·5	0·05 M barbital	607(18·9)	none	428(79)	4·2
Pyridine (20% v/v)	13	0·1 N NaOH	587(29·2-31·0)	none	430(117)	4·6
	9	0·5 M borate	587(29·9)	none	430(115)	3·8
		water	587(24·8)	530(10·5)	429(91)	3·7
Pyridine (20% v/v) + CO	13	0·1 N NaOH	592(17·1)	none	429(117)	6·9
4-Methyl imidazole (2%)	9	0·05 M borate	594(22·2)	520(10·8)	441(70)	3·3
4-Methyl imidazole (2%) + CO	9	0·05 M borate	605(19·0)	none	435(57)	3·0
NH3 (2%)	—	—	592·5(21·3)	none	435(77)	3·6
Cyanide (0·1 M)	13	0·1 N NaOH	598(23·0)	534(10·9)	446(101)	4·4
Native human globin (1%)	9	0·05 M borate	595(24·7)	none	442(103)	4·2
Native human globin (1%) + CO	9	0·05 M borate	602·5(22·0)	none	432(126)	5·7
Apoperoxidase (0·5%)	9	0·05 M borate	596(15·6)	none	441(93)	5·9
Apoperoxidase (0·5%) + CO	9	0·05 M borate	601(14·8)	550(10·8)	432(93)	6·3
Human serum albmin (0·5%)	9	0·05 M borate	590(20·3)	none	435(91)	4·5
Human serum Albumin (0·5%) + CO	9	0·05 M borate	596(15·1)	542(13·2)	429(133)	8·8
	7·5	0·05 M barbtial	599(14·2)	575(13·0) 540(12·6)	420(101)	7·1
Ox serum Albumin (0·5%)	9	0·05 M borate	590(25·2)	540(11·1) 510(11·0)	435(93)	3·7
	7·5	0·05 M barbital	589(19·4)	540(11·2) 512(10·8)	428(69)	3·6
Ox serum Albumin (0·5%) + CO	9	0·05 M borate	600(20·0)	none	431(102)	5·1
	7·5	0·05 M barbital	600(15·0)	545(11·8)	417(97)	6·5
Denatured globin (1%)	13	0·1 N NaOH	575(19·4)	530(11·7) 505(11·7)	429(101)	5·2
Denatured globin (1%) + CO	13	0·1 N NaOH	584(15·1)	545(12·2)	424(147)	9·8
Denatured ox serum albumin (0·5%)	13	0·1 N NaOH	573·5(25·4)	530(14·1)	430(118)	4·6
Denatured ox serum albumin (0·5%) + CO	13	0·1 N NaOH	583(18·0)	452·5(16·4)	423·5(155)	8·6
Denatured human serum albumin (0·5%)	13	0·1 N NaOH	574	530 505	430	

3.3 SPECTROSCOPY OF CARBON VAPOR

While some of the theories on interstellar grains are outlined in
Technical Report I, it might be worthwhile to review at this point the
situation with graphite and all carbon-vapor deposited on rare gas
matrices, since the graphite hypothesis is in vogue at the present time.

Referring to a paper by Weltner et al[*], we reproduce their curves
showing the absorption spectra of carbon vapor in neon and argon
matrices at $4°K$ (Fig. 22). Note that none of the absorption lines
corresponds even remotely with the diffused interstellar lines, al-
though the sharpness of the lines shows up interestingly enough.
Furthermore, the effect of substrate matrix on the position of the
absorption band is rather severe, as shown in Table VI, where compari-
sons are made for neon, argon, and xenon, showing that these matrix
shifts could be as much as $100Å$. It is hard to see how any theory is
tenable that relies on impurity atoms deposited in matrices in view
of these large possible shifts that could be obtained.

TABLE VI

SWAN-BAND TRANSITIONS OF C_2 IN INERT-GAS MATRICES AT $4°K$

Matrix	Observed transition		
	(0'-0'')(Å)	(1'-0'')(Å)	$\Delta G'_{\frac{1}{2}}(cm^{-1})$
gas[a]	5165	4737	1750
neon	5110	4616	2094
argon[b]	5202	4700	2053
xenon[c]	5270	4781	1940

[a] G. Herzberg, <u>Molecular Spectra and Molecular Structure I, Spectra of Diatomic Molecules</u> (D. Van Nostrand Company, Inc., New York, 1950)

[b] M. McCarty and G. W. Robinson (J. Chim. Phys. <u>56</u>, 723 (1959)) found 5207 and 4727Å in argon

[c] M. McCarty and G. W. Robinson, Mol. Phys. <u>2</u>, 415 (1959)

[*] W. Weltner et al, J. Chem. Phys. <u>40</u>, 1299 (1964)
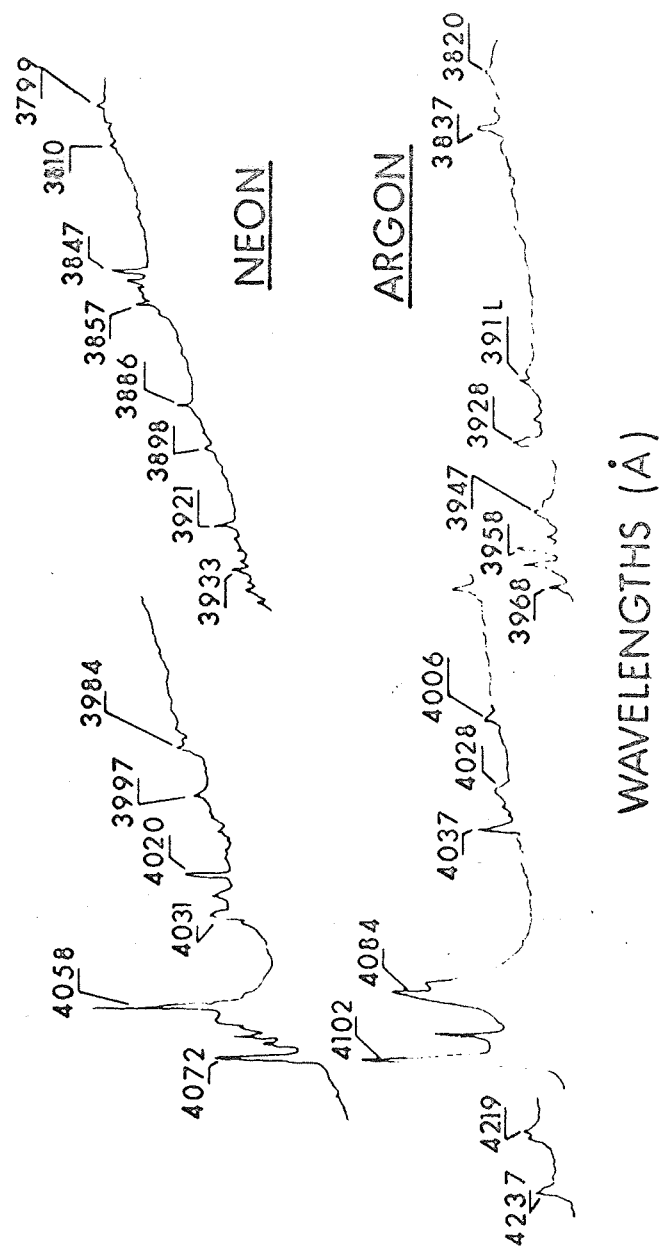
Figure 22. Absorption Spectra of Carbon Vapor in the Near Ultraviolet in Neon and Argon Matrices at 4° and $20^\circ K$

27958

3.4   SPECTRA FROM RARE-EARTH IONS

Figure 23 shows the energy level diagram for rare-earth ions in anhydrous chlorides, taken from G. H. Dieke.   It shows many potentially narrow lines possible from these rare-earth compounds.   Although no precise match with the diffuse interstellar lines has been found using these ions, the main reason for excluding these ions for components in the interstellar dust particles is based on the fact that the cosmic abundance is so very low (see Report No. 1) and, too, the oscillator strengths for the transitions are generally low.   We include this information for the sake of completeness, in the unlikely event that some unforeseen, anomalous high rare earth abundance in the interstellar medium could exist, perhaps as a result of fission reactions.

Figure 23. Energy Levels of the Trivalent Rare-Earth Ions as Found for Their Anhydrous Chlorides
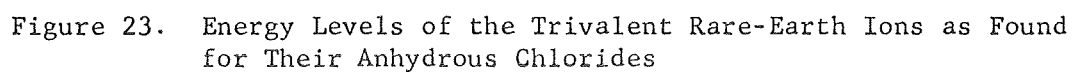
SECTION 4
DIFFUSE INTERSTELLAR LINES AND THE INTERSTELLAR DUST GRAINS

A discussion of the basic properties of the dust grains as well as
references was given in Scientific Report No. 1. Figure 24, kindly
supplied by Dr. G. Herbig, shows part of the spectrum of 6 hot back-
ground stars with spectral designation ranging from blue O6 to essen-
tially white B7. These stars were chosen mainly because of their
great intrinsic brightness and consequent limited stellar spectral
lines. Superimposed on the stars' spectrum are the interstellar lines
and bands. The sharp interstellar Na D lines are used as a frequency
reference, allowing the Doppler shifts due to the random velocities
of the interstellar dust clouds to be subtracted. The strongest dif-
fuse line at 4428Å does not appear on this photograph; however, the
next strongest lines at 5780Å and 6284Å appear quite clearly.
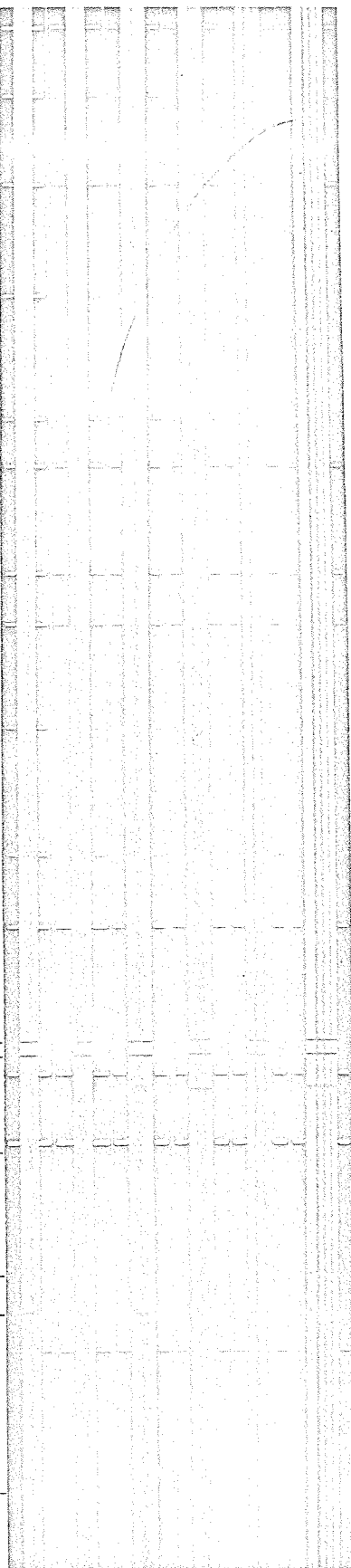
Figure 24. Diffuse Interstellar Absorption Lines for Six Background Stars (from G. Herbig)

4.1 THE KRAMER-KRONIG RELATIONS AND THE INTERSTELLAR DUST

In this section we wish to discuss the relationship between absorption and dispersion. Although the absorption measurements play a dominant role in the interpretation and analysis of the dust grains, one usually neglects the fact that absorption and dispersion are connected via the Kramer-Kronig relations.

$$K(\omega) - 1 = \frac{2C}{\pi} \int_0^\infty \frac{\omega' \gamma(\omega') d\omega'}{\omega(\omega'^2 - \omega^2)}$$

$$\gamma(\omega) = \frac{-2\omega^2}{\pi C} \int_0^\infty \frac{[K(\omega') - 1] d\omega'}{\omega'^2 - \omega^2}$$

where

$$K = \text{Dielective constant}$$
$$\gamma = \text{Absorption coefficient}$$

Unpublished data, kindly made available by Dr. C. R. O'Dell of Yerkes Observatory, and shown in Fig. 25, comprises reflection data from an extended dust cloud, illuminated in the forefront by a highly luminous star. The emission features at 4340, 4387, and 4471 are seen quite clearly. The position of an expected feature at 4430 is shown by an arrow. Since the reflection coefficient R is given by the following formula,

$$R = \frac{(n-1)^2 + m^2}{(n+1)^2 + m^2}$$

then the knowledge of the real and imaginary parts, n and m, of the reflective index can be used to compute the reflection coefficient. The data unfortunately is inconclusive but suggestive that such a feature could exist in this reflective dust cloud. A signal-to-noise improvement by a factor of three would be necessary to make an unambiguous assignment. If this would be the case, one could then deduce from experimental data that bulk properties of the dust, and not impurities imbedded in the
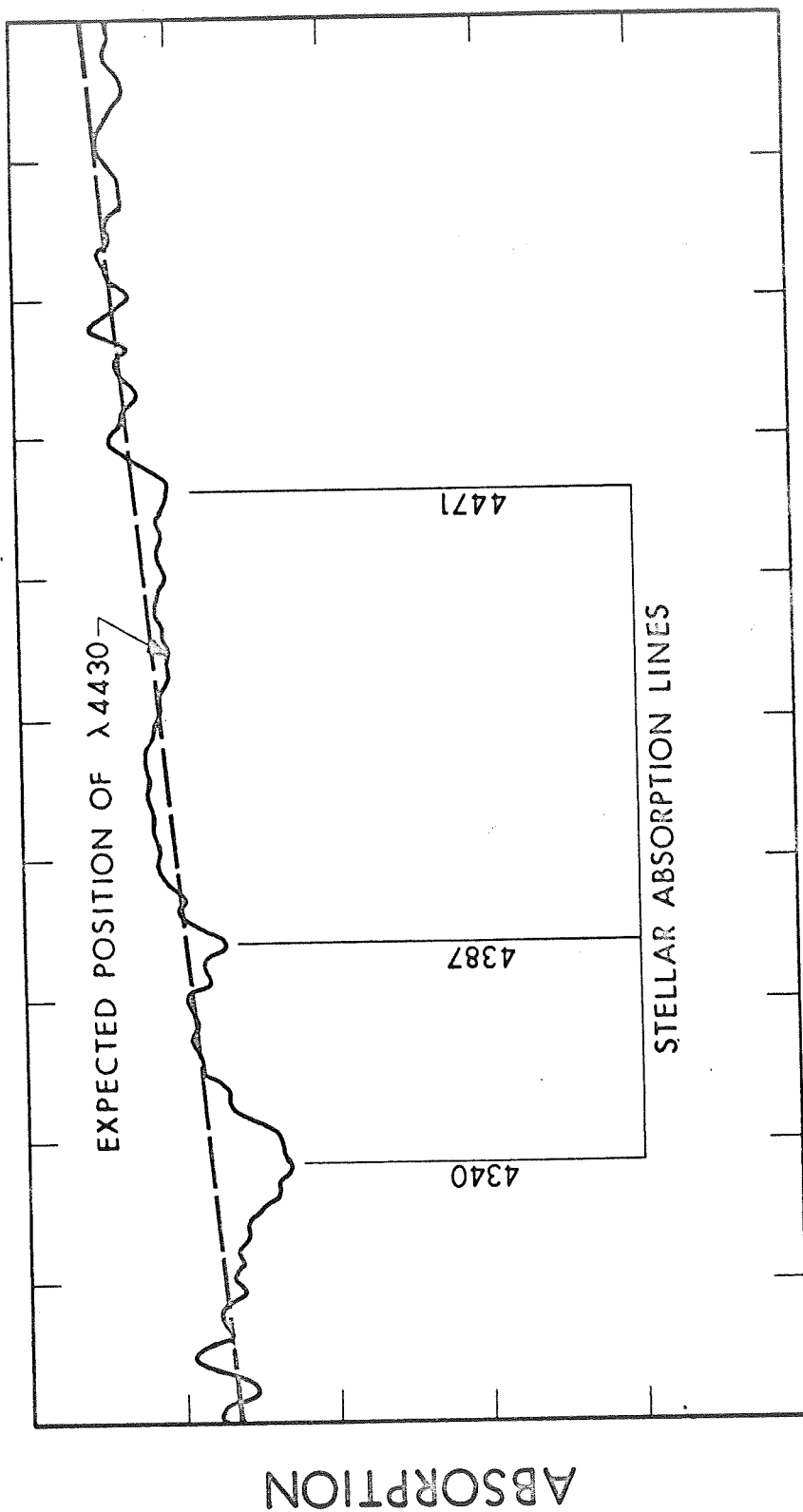
7129-Final

Figure 25.   Reflection Data from an Extended Dust Cloud

grain, are responsible for the diffuse interstellar lines. This information, by itself, would invalidate a large number of theories based on the "impurity-in-the-matrix" concept, which could be discarded on other grounds, as discussed previously.

4.2 ORIGIN OF INTERSTELLAR DUST

The theory that we propose on the origin of the interstellar dust is connected with the M-type variable stars. These stars can be surrounded by shell-like structures and are associated with extreme variations in light intensity, polarization, and the angle that this polarization vector makes as a function of time.[*] The details of this model will be outlined in greater detail in Phase II of the follow-on program. However, we shall sketch out the main outlines of the theory in this report.

We suppose that the central, M-type variable star emits carbon, hydrogen, nitrogen, and other atoms in a manner similar to that of the solar wind. This molecular beam and atomic gas streaming will allow condensations to take place on cooler portions of the inside of the shell surrounding the star. The shell of the star can obviously not be solid, since paths must be allowed for venting the large amount of radiation produced by the M-type star. Furthermore, large temperature variations must be present on this shell--hot on the inside and cool on the outside--and since it is porous, it will presumably allow for variations in possible accretion and growth mechanisms. The interstellar grains formed on these shells are blown off periodically (whether because of the periodic M-type star instability or as a result of clogging up of the pores of the shell, or both). In any event, it looks very promising at the moment that this type of shell structure could be surrounding these cooler M-type stars, particularly since the infrared radiation that is being astronomically observed is thought to be due to the large dust clouds surrounding a central star. The fact that polarization of starlight on these objects can be observed is a distinct characteristic of the dust grains. The mechanism for lining up these dust grains still needs to be worked out. It could possibly be due to the central star's own magnetic field.

---

[*] R. R. Zappala, "Fluctuating Polarization in Long-Period Variable Stars," Ap. J., 1967 (See Figs. 26 and 27 for data from this paper)
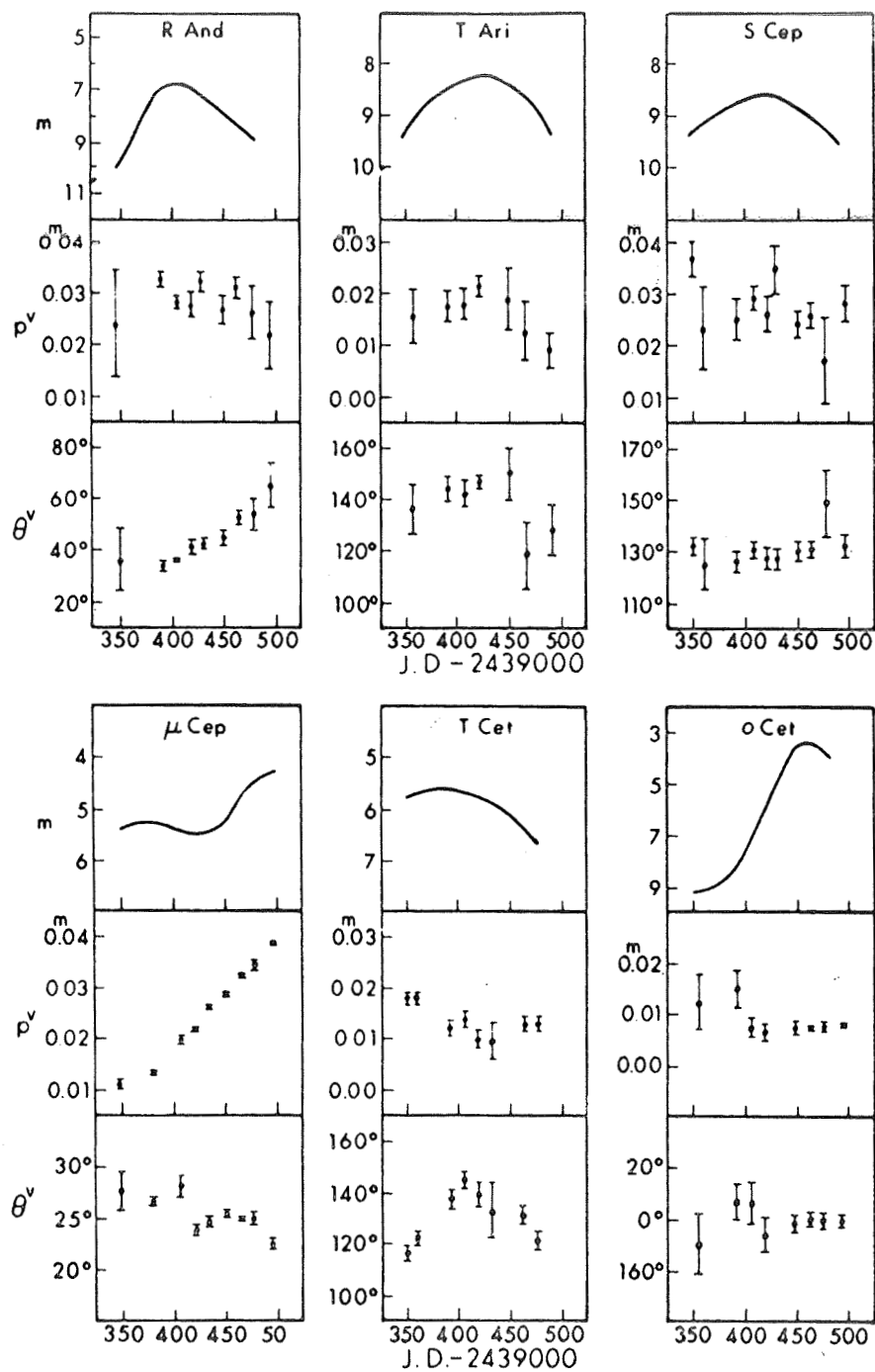
Figure 26. Polarimetric Observation of Six Variables.
Error Bars Indicate Standard Deviations
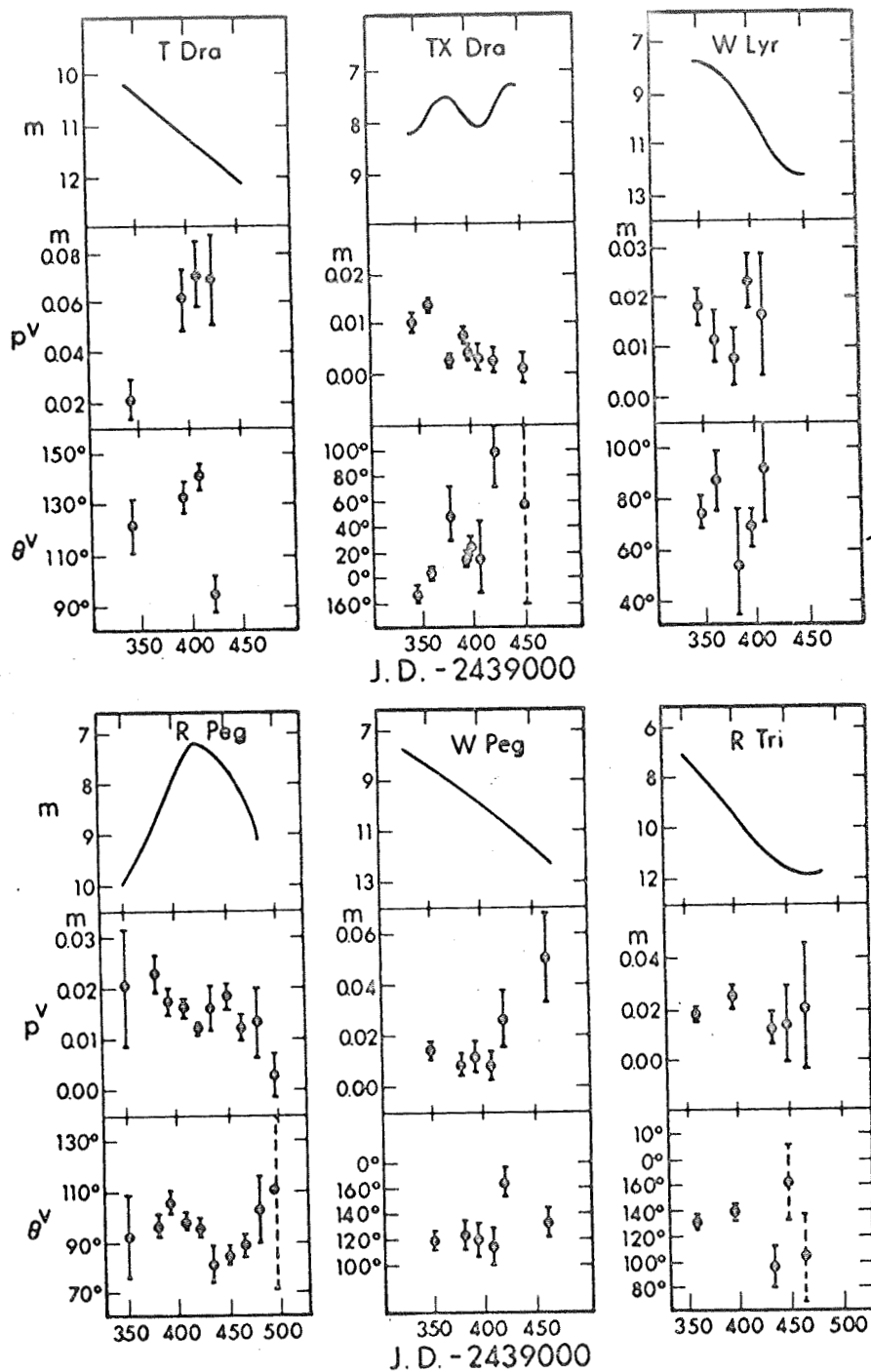
Figure 27. Polarimetric Observations of Six Variables.
Dashed Error Bar for θ^V Indicates an Error
in Polarization Larger Than the Polarization
Itself

It is interesting to note that some of the IR stars[*] do indeed have intensity variations with periods greater than 400 days and are in fact known (M) Mira-type variables.[**]

A theoretical model developed by Stein describes infrared emission by a circumstellar dust cloud. If the flux from the star at the earth is given by

$$B_{star} = \frac{2\pi hc^2}{\lambda^5} \; 4\pi \frac{R_*^2}{D^2} \; \frac{1}{\exp\left[\frac{hc}{\lambda k T_*} - 1\right]}$$

and the energy (B_{cl}) received at the earth per unit wavelength interval from a shell of thickness dR at a distance R from the star

$$B_{cloud} = \frac{4\pi R^2 dR}{4\pi D^2} \int F(\lambda, T_p) \; 4\pi r^2 n(r,R) dr$$

then, a set of parametric curves can be drawn for various shell radii R as shown in Fig. 28 taken from Stein.

$F(\lambda, T_p)$ is the energy per sq cm per sec per unit wavelength emitted by the dust grain.

D = distance from earth to star

$4\pi R^2 ndR$ = number of grains of radius r in the shell

$n = n_o \dfrac{R_{max}}{R}$, where R_{max} = radius of circumstellar cloud

n_o = number density of particles of size r at distance R_{max} from the star

---

[*] See, e.g., H. L. Johnson, F. J. Low, and D. Steinmetz, Ap. J. _142_, 808 (1965)
[**] R. F. Wing, H. Spinrad, and L. V. Kuhi, Ap. J. _147_, 117 (1966)
B. T. Ulrich, G. Neugebauer, D. McCammon, R. B. Leighton, E. E. Hughes, and E. Becklin, Ap. J. _146_, 288 (1966)
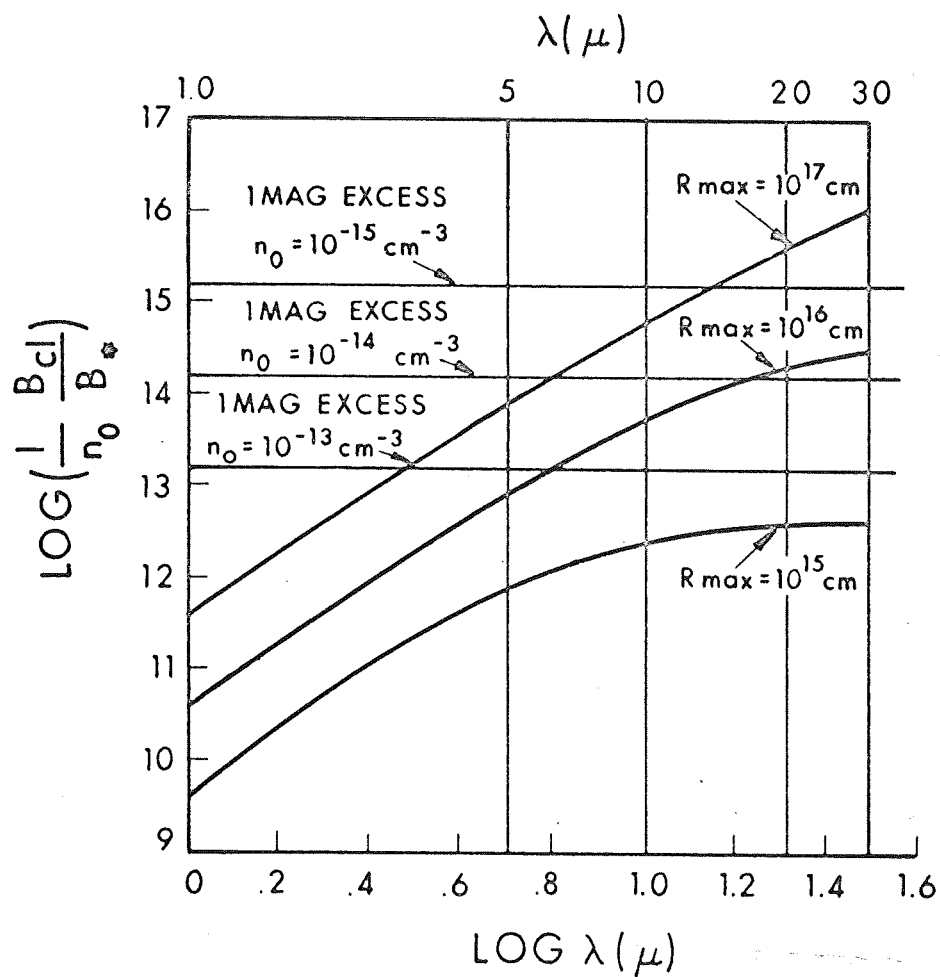
Figure 28. The Ratio of the Brightness of the Circumstellar Cloud to the Stellar Brightness as a Function of Wavelength for a Star with T = 10,000°K; N_0 is the Density of Grains with Radius 2.5μ at a Distance R_{max} from the Star

7952

The conclusion reached by Stein was that if the dust density near these stars is of the order of 1000 times more dense than average interstellar density, then the IR excess observed by some stars can be attributed to emission by these grains.

4.3 CONCLUDING REMARKS ON THE ASTRONOMICAL DATA

The bulk of the astronomical reference data is either referred to or discussed in Scientific Report No. 1. Three additional remarks need be made here:

(1) There is a general correlation of intensities of all the diffuse interstellar lines.[*] A specific example is shown in Fig. 29 from a figure taken by Walker,[**] where the 4430Å intensities as ordinates (marked C on the curve) are plotted against the 5780 and 6284 lines.

(2) There is a distinct possibility that polarization may be associated with the 4430 line (G.A.H. Walker). This would be an important clue, consistent with known porphyrin data. This point needs further study.

(3) It is interesting to note that Platt[+] developed a model for interstellar dust grains in 1955 which utilized the theory described in Section 2. His model was rather specialized and yielded absorption wavelengths as a function of molecular diameter, ℓ. The energies were given by

$$E_\ell = \frac{h^2}{8m} \frac{2n_L}{\ell^2}$$

The result is plotted in Fig. 30.

---

[*] G. Herbig, private communication

[**] G. A. H. Walker, M. N. 125, 141 (1963)

[+] John R. Platt, Ap. J. 123, 486 (1956)
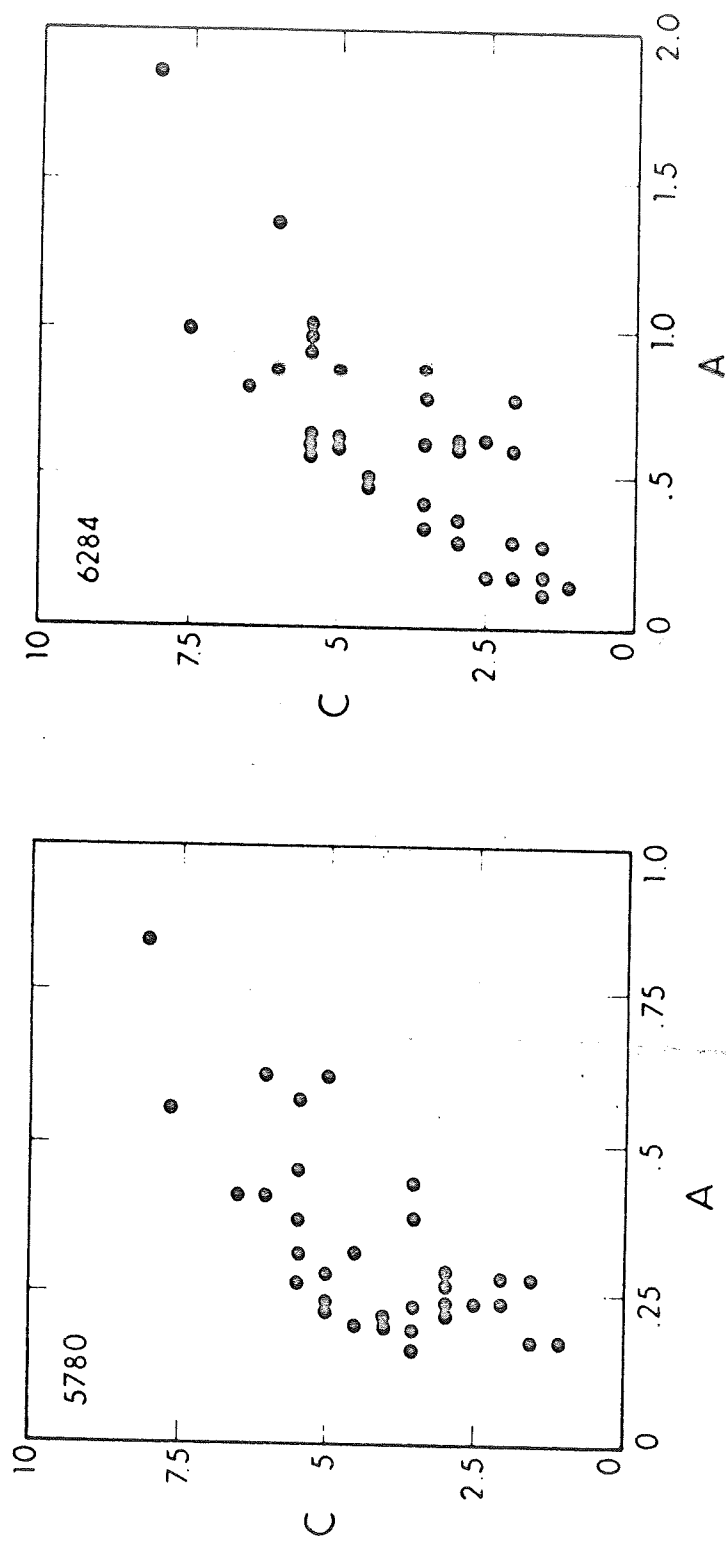
Figure 29. Correlation of Cambridge 4430 Measures (C) with the Intensities of the 5780 and 6284Å Diffuse Interstellar Features
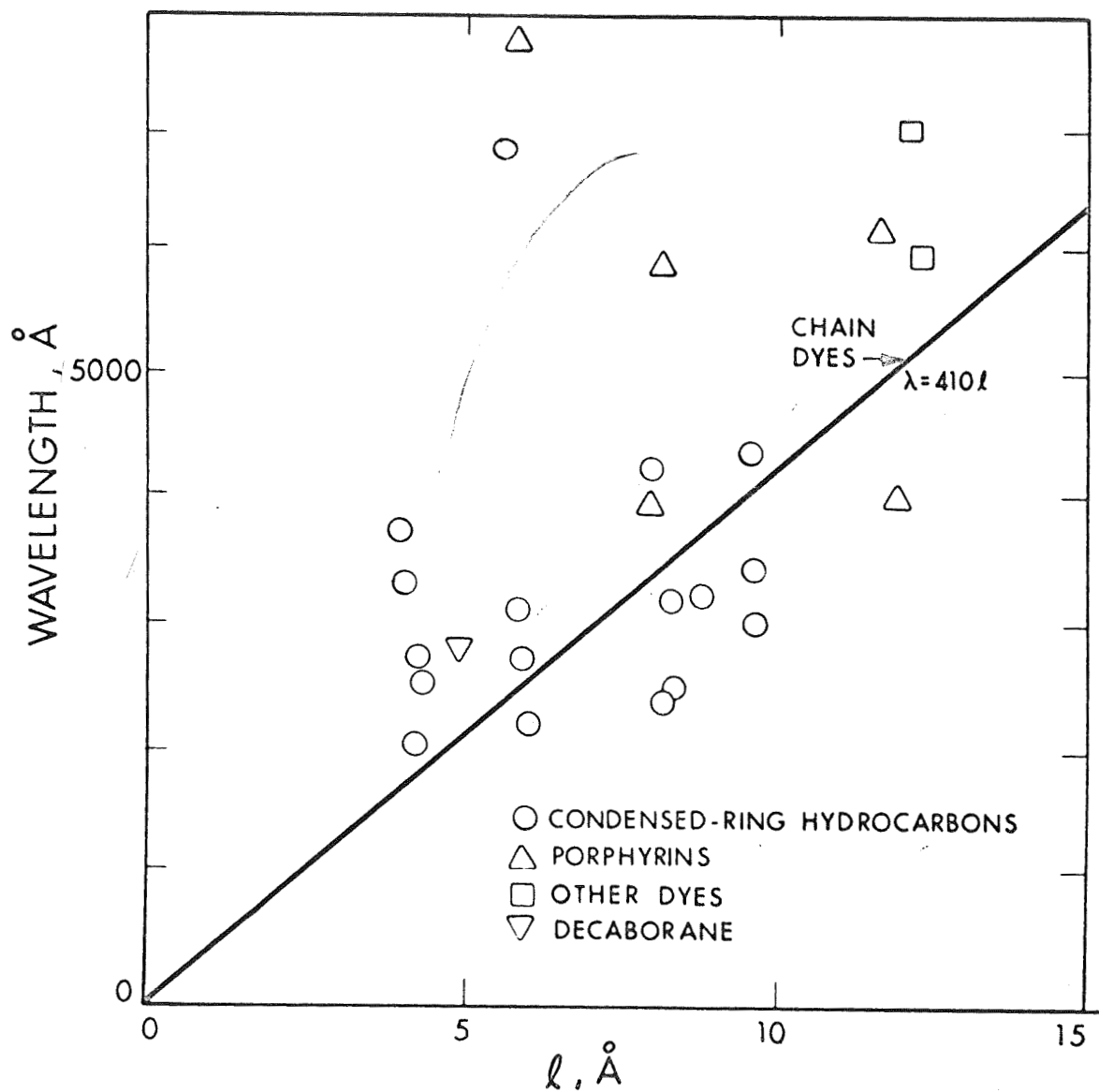
Figure 30. First Absorption Wavelengths versus Molecular Diameter Parallel to the Direction of Polarization for Molecules with Unfilled Energy Bands

It is a curious coincidence that Platt plots, for one of the points, the PORPHYRIN molecule.

The difference between Platt's model and ours is that the former was developed for "abstract" particles of less than 10Å in size, whereas our model requires grains consisting of a large number of porphyrin type molecules.

ABSORPTION DATA

In concluding this report, a number of pages taken from Falk are presented, showing the main absorption bands for a number of porphyrin compounds as well as the strength of the absorption band. These tables are included to show the differences resulting from solvent effects as well as the slight variations in the chemical formula for the porphyrins. Note chlorophyll c, whose absorption bands are very suggestive, as well as the haem wavelength. These tables are not all inclusive but only suggestive. Much more data exists, but very little at $4^{\circ}K$. This is why it is imperative to repeat these measurements in a cold-finger arrangement, as has been proposed in a follow-on program.

TABLE VII

ABSORPTION SPECTRA OF CHLOROPHYLL DERIVATIVES

Compound	Solvent	λ_{max} (mμ) α^* and ε_{mM}	350– 380	380– 400	400– 420	420– 450	450– 500	500– 520	520– 550	550– 580	580– 600	600– 650	650– 700	700– 800
Chlorophyll a	*Ether	λ			410	430			533.5	578		615	662	
		α			85.2	131.5			4.22	9.27		16.3	100.9	
	Acetone (80%)	λ				433			536		582	618	665	
		α				101.5			4.78		11.6	19.6	90.8	
Chlorophyll b	*Ether	λ				430	455		549		595	644		
		α				62.7	174.8		7.07		12.7	62.0		
	Acetone (80%)	λ					460		(536)	(558)	600	648.9	(665)	
		α					148.0		(6.37)	(7.91)	14.3	52.5	(10.8)	
Chlorophyll c	*Ether	λ				447				579.5		*628		
		α				227.0				20.6		22.0		
	Acetone	λ				442				580		*628		
Chlorophyll d	*Ether	λ		392		447		512	548.5		595	643	688	
		α		58.9		97.8		1.98	4.03		9.47	14.3	110.4	
Bacteriochlorophyll	*Ether	λ	358.5	391.5					(530)	577			(697)	773
		α	80.5	52.8					(3.0)	22.9			(10)	100
	Methanol	λ	365									608	(685)	772
		α	59.2									16.9	(9.5)	46.1
Phaeophytin a	*Ether	λ			408.5		471	505	534	560		609.5	667	
		α			132.0		5.1	14.6	12.6	3.6		9.8	63.7	
	Dioxan	λ						506	535	559		609	667	
		ε_{mM}						10.1	8.65	3.2		6.98	43.0	
	Acetone (80%)	λ			409		472	505	536	(558)		610	666–667	
		α			130.9		6.3	15.0	13.12	(5.23)		11.9	56.6	
Methyl phaeophorbid a	Dioxan	λ						506	535	560		610	666	
		ε_{mM}						11.04	9.27	2.84		7.77	52.76	
Chlorin a₆ (e₆) methyl ester	Dioxan	λ						500	529	559		610	664	
		ε_{mM}						13.2	5.21	2.0		4.09	53.25	
Chloroporphyrin a₆ trimethyl ester	Dioxan	λ						506	543	576		629		
		ε_{mM}						12.63	8.09	6.73		1.7		

*Smith, J.H.C., and A. Benitez in K. Paech and M. Tracey (eds.), Modern Methods of Plant Analysis, Vol. 4, Springer, Berlin, 1955, p. 142

TABLE VIII

PORPHYRINS IN ORGANIC SOLVENTS

Porphyrins	Solvent	λ_{max} (mμ) ε_{mM}	Soret	IV	III	II	Ia	I
Uro I and III octa methyl ester	CHCl₃	λ	406	502	536	572		627
		ε	215	15.8	9.35	6.85		4.18
	Dioxan	λ		499	531	569	596	624
		ε		15.25	9.26	6.99	1.39	3.93
Copro I and III tetramethyl ester	CHCl₃	λ	400	498	532	566	594	621
		ε	180	14.34	9.92	7.13	1.48	5.0
	Ether	λ	397	498	527	568	596	623
		ε	172	15.12	10.58	7.27	1.32	6.69
	Pyridine	λ	401.5	498	531	567	595-6	622
		ε	173	15.05	10.06	7.28	1.72	5.15
	Dioxan	λ	398	497	530	566	595	621
		ε	177	15.35	10.3	7.24	1.4	5.41
Proto IX dimethyl ester	CHCl₃	λ	407	505	541	575	603	630
		ε	171	14.15	11.6	7.44	2.03	5.38
	Ether	λ	404	503	536	576	605	633
		ε	158	14.8	11.86	6.63	1.54	6.57
	Pyridine	λ	409	506	541	576	605	631
		ε	163	14.89	11.87	7.48	2.0	5.54
	Dioxan	λ	406	504	538	575	603	631
		ε	164	14.7	11.59	6.86	1.41	5.60
Deutero IX dimethyl ester	CHCl₃	λ	399.5	497	530	566	593	621
		ε	175	13.36	10.1	8.21	2.21	4.95
	Ether	λ	395	492	524	566	595	621
		ε	170	14.04	8.61	6.19	1.24	5.18
	Pyridine	λ	400	497	529	566	593	620
		ε	175	14.5	7.84	6.32	1.32	3.85
	Dioxan	λ	397	495	525	565	593	618
		ε	170	15.95	8.59	6.8	1.29	4.33
Meso IX dimethyl ester	CHCl₃	λ	400	499	533	567	594	621
		ε	166	13.56	9.62	6.48	1.69	4.87
	Ether	λ	395.5	497	526	567	596	623
		ε	158	13.81	10.21	6.64	1.35	6.64
	Pyridine	λ	401	498	532	567	595	621
		ε	160	14.37	10.0	6.92	1.68	5.2
	Dioxan	λ	397	497	529	567	595	621
		ε	166	14.29	9.67	6.56	1.36	5.36
Haemato IX dimethyl ester	Pyridine	λ	402	499.5	532	569.2	596	623
		ε	175.5	14.7	9.04	6.57	1.26	4.35
Aetio I	CHCl₃	λ	399.5					
		ε	160					
	Dioxan	λ		496	528	566	595	621
		ε		13.6	9.5	5.95	1.36	5.18
2(4)-Monoformyl-deutero IX dimethyl ester	Ether	λ		510.5	550.5	578		640.5
	CHCl₃	λ		515	555	580		641
		Ratios		1.0	1.79	1.037		0.175
	Dioxan	λ		512	551	578.5		640
		Ratios		1.0	1.43	0.85		0.223
2,4-Diformyl-deutero IX dimethyl ester	Ether	λ		521	557.5	593		648
		λ	435	526	562.5	595		651
	CHCl₃	ε	137.5	12.6	7.70	6.48		3.48
		Ratios	10.9	1.0	0.61	0.51		0.28
	CHCl₃	λ	437	527	563	596		650.5
		Ratios	10.12	1.0	0.58	0.47		0.265

SECTION 6
LITERATURE SURVEY

INTRODUCTION

Part of the contractual requirement of the interstellar dust program
was to conduct a comprehensive literature survey. Since the exact nature
of the chemical compounds associated with the interstellar dust is un-
known, the library search included a somewhat wider field of materials
than ordinarily would have been undertaken. The underlying theory was
as follows: Since none of the simpler molecules, including thousands
of simple hydrocarbon compounds, show spectra even remotely suggestive
of interstellar absorption line features, it was decided to concentrate
on the more elaborate porphyrin and related compounds. The subjects
were eventually widened to include not only the porphyrins but the
carotenoids, pyrroles, flavins, cytochromes, and other biochemically
active compounds. The reason for this choice is the fact that the spectra
of these compounds show absorption lines in the visible region and near
the uv region, some of which appear suggestive as possible candidates
for the interstellar absorption lines.

In compiling this bibliography, emphasis was placed on obtaining ref-
erences which contain spectra and, if possible, spectra taken at low
temperatures. It soon became apparent that other factors in addition
to temperature entered into the position of the maxima, namely, con-
centration, pH, dryness, material preparation and purity with the crystal-
line or liquid matrix in which the material was contained, vivo, vitro,
and sometimes even the observer.

It was found that a great deal of the literature is worldwide in origin, furthermore, since it crosses into four disciplines (biology, chemistry, physics, and astronomy) and the cross fields (such as biochemistry, etc.) the search became increasingly difficult. Conversely, it is hoped that this bibliography may be of use to exobiologists as well as other workers in the field.

The library search included other phenomena related to these compounds such as ESR, EPR, NMR, fluorescence, infrared spectra, photosynthesis, and biochemical processes. Since the amount of material obtained would, in itself, constitute a report of some bulk, some selection was exercised in the choice of references cited.

WARNING:

The presence in this literature survey of a large number of biochemically active materials does not necessarily imply that they should all, or any of them, be present as constituents of interstellar dust. The references were used such that the spectra could be analyzed and serve as guideposts for further comparison and research, using the known diffuse interstellar lines as touchstones throughout the search. A more detailed discussion of these points is contained in Section 3.

NOTES ON THE BIBLIOGRAPHY

All abstracts were obtained from the Chemical Abstracts and are designated in the right upper corner in order of volume, page and year. The numbers above the CA reference refer to the subject index of this bibliography (see key). The material was divided into 18 categories involving measurement techniques, compounds and theory. Subjects which did not fit any category were placed in category No. 13 (general). Two or more categories are usually used to describe the content of the

article. Although a very exhaustive literature search was undertaken, some selection was exercised for final insertion in this compilation. Entries up to December 1966 are included.

KEY TO SUBJECT INDEX

1. Spectra (mainly absorption)
2. Porphyrins
3. Carotenes
4. Phthalocyanines
5. Cytochromes
6. Astronomy
7. Pyrroles
8. Flavins
9. Haems
10. Theory
11. Biology
12. Photosynthesis
13. General, incl. chemistry, dyes
14. IR
15. Fluorescence, bioluminescence
16. ESR (EPR), NMR, mass spectrometry, magnetic susceptibility, γ-rays
17. Chlorophyll
18. Optical rotatory dispersion, polarization

Albrecht, Andreas

Polarizations and assignments of transitions: the method of photo-
selection. (Cornell Univ., Ithaca, N.Y.). J. Mol. Spectroscopy
6, 84-108 (1961). An outline is given of the theory, which underlies
the concept of the polarization of an electronic transition. Nuclear-
coordinate-dependent electronic functions are employed to bring out
the significance of mixed polarization in an electronic absorption or
emission band. The method of photoselection includes polarized emis-
sion studies and polarized photochemistry. The theory underlying the
method is outlined. A table of ideal orientation ratios for a variety
of conditions is presented. Practical application of the theory is
examined and it is shown how (and under what conditions) it is possi-
ble to relate gross observations to intrinsic mol. anisotropy of
absorption (or emission). Two specific examples are analyzed, 1 in-
volving polarized emission, the other polarized photochemistry. When
polarization of phosphorescence and fluorescence measurements are made
together, addnl. information can be provided with regard to anisotropy
in absorption, which is not available when only 1 of the 2 types of
measurements is made.

Allen, Wallace and Latimer, Paul

Anomalous dispersion of β-carotene solutions. (Vanderbilt Univ.,
Nashville, Tenn.). J. Opt. Soc. Am. 52, 192-6 (1962). Refractive
indexes were detd. by measurement of reflectance at a glass liquid
interface, transmittance of the liquids, and calcn. of relative in-
dexes from a reflection equation. The spectral region of 4000-5890
A. includes 4 absorption bands of β-carotene.

Allison, Jean B. and Becker, Ralph S.

Effect of metal atom perturbations on the luminescent spectra of
porphyrins. (Univ. of Houston, Houston, Tex.). J. Chem. Phys. 32,
1410-17 (1960). The low-temp. emission spectra of the dimethyl ester
of mesoporphyrin IX and its bivalent derivs. of Co, Ni, Cu, Zn, Pd,
Cd, and Ba were obtained. Mg etioporphyrin II and Zn phthalocyanine
were also investigated. The bivalent Ag mesoporphyrin was also
studied, but no luminescence was obtained. Considerations of the
relative lifetimes of fluorescence and phosphorescence of the various
derivs. permit qual. deductions to be made regarding magnetic suscepti-
bility. Anomalous emission characteristics of several of the metallo-
porphyrins were tentatively interpreted in terms of crossing of a 1st
excited state and the ground state.

Anderson, A.
1, 17
CA 60-7069e (1964)

Some new molecular biology of chlorophyll a. (Univ. of California,
Berkeley). U.S. At. Energy Comm. UCRL-10951, 145 pp. (1963). Cryst.
chlorophyll a and Me chlorophyllide a were prepd. by column chroma-
tography on powd. polyethylene and (or) sucrose. Changes in the
shapes of the red and blue bands of the chlorophyll a in CCl_4 soln.
occurred at different concns. and suggested the existence, in concd.
solns., of nonspecified solute-solute interactions. Infrared spectra
of chlorophylls a and b in nonpolar solvents revealed weak carbonyl-
Mg interactions. NMR spectra of chlorophylls a and b and of Me
pheophorbide a are given. Chem. shifts of $\delta = 7.5-5.95$ and $\delta = 8.5-8.1$
were found for the protons at C-10 and at the δ bridge carbon atom.
Preliminary electron spin resonance studies on plant exts. and chloro-
phyll a showed H_2O to be requisite to the production of signals from
the exts. and the purity of the chlorophyll a to affect the signal ob-
tained.

Anderson, A. F. H. and Calvin, Melvin
1, 13,17
CA 57-2568g (1962)

Improved method for the separation and purification of chlorophyll a.
(Univ. of California, Berkeley). Nature 194, 285-6 (1962). Spinach
(200 g) is extd. with 500 ml. acetone and dild. with water to give an
80% water-acetone soln. The ext. is chromatographed on a 5 cm glass
column packed with 1000 ml. polyethylene (Dow M 1 < 2) and washed with
70% aq. acetone to remove the bottom layer of xanthophyll. Chloro-
phylls a and b eluted with 85% aq. acetone are extd. with isooctane
and dried on Na_2SO_4. The soln. is then chromatographed on a 5-cm
glass column packed with 1000 ml. of confectioner's sugar and eluted
with 0.5% PrOH in isooctane, yielding chlorophyll a, which is refriger-
ated to crystallize. The powder has a defined x-ray pattern and spec-
trum at 740 mμ. Yield is 40 mg.

Anderson, Joan Mary
13, 12, 3, 17
CA 55-13566e (1961)

Research in photosynthesis. I. Biosynthetic studies on the chloro-
phylls and carotenoids of algae. (Univ. of California, Berkeley).
U.S. At. Energy Comm. UCRL-8870, 1-113 (1959).

Anderson, J. M.; Blass, U. and   1, 3, 13, 17
Calvin, Melvin   CA 55-4597a & d (1961)

Biosynthesis and possible relations among the carotenoids and between chlorophylls a and b. (Univ. of California, Berkeley). Ibid. 215-25. Comparative Biochemistry of Photoreactive Systems (V.1 of Symposia on Comparative Biology) Mary Belle Allen, ed., New York Academic Press, 1960.

Anderson, J. S., Bradbrook, E. F.,   4, 1
Cook, A. H. and Linstead, R. P.   CA 32-84231 (1958)

Phthalocyanines and associated compounds. XIII. Absorption spectra. J. Chem. Soc. 1938, 1151-6; cf. C. A. 31, 6237[8]. The absorption spectra in the visible region of phthalocyanine (I), 15 of its metallic derivs. and a no. of assocd. compds. contg. the tetrazaporphin (porphyrazine) ring have been measured. The spectrum of I is composed of a system of at least 7 bands, the main absorption occurring between 6000 and 7000 A.

Armstrong, J.   4,13
     CA 62-15600e (1965)

Saturable optical absorption in phthalocyanine dyes. (Intern. Business Machines, Yorktown Heights, N.Y.). J. Appl. Phys. 36 (2), 471-3 (1965) (Eng). An exptl. study is reported of the satn. of optical absorption at 6943 A. of chloroaluminum phthalocyanine dissolved in chloronaphthalene and of V phthalocyanine dissolved in $PhNO_2$; a giant ruber laser is used as the source of intense resonance radiation. This absorption transition occurs between the singlet ground state and the lowest-lying excited singlet and has a molar absorptivity of the order of 300,000.

Arnon, Daniel I.   13
     CA 55-13485h (1961)

Cell-free photosynthesis and the energy-conversion process. (Univ. of California, Berkeley). Ibid. 489-565. IN: Symposium on Light and Life, Johns Hopkins University, 1960. Light and Life; proceedings. Edited by William D. McElroy and Bentley Glass. (Johns Hopkins University. McCollum-Pratt Institute. Contribution No. 302)

Aronoff, S.

<div align="right">1, 17
CA 45-449b (1951)</div>

<u>Absorption spectra of chlorophyll and related compounds</u>. (Iowa State Coll., Ames). Chem. Revs. 47, 175-95 (1950). Absorption spectra of chlorophyll and homologous compds. are described qualitatively. Brief discussions are included of the contribution of polar species to the ground state, the influence of the spatial orientation of the substituent on the spectra, chelate and acid vs. free-base spectra, fluorescence, and phosphorescence, and the initial contemporary analyses of the band structure.

Aronoff, S.

<div align="right">1, 17
CA 46-6211d (1952)</div>

<u>Light absorption by chlorophyll at high concentrations</u>. (Iowa State Coll., Ames). Plant Physiol. 27, 413-16 (1952); cf. C.A. 45, 449b. Increasing the concn. of chlorophyll in solns. did not shift the position of the red absorption max. to coincide with that for the living tobacco leaf. There is apparently no solvent in which chlorophyll has the same region of max. absorption as it has in the leaf. Probably chlorophyll is assocd. with some substance in the leaf. Synthetic chlorophyll-protein complexes may also be made which exhibit most of the soly. characteristics assocd. with the biol. system.

Assour, Jacques M.

<div align="right">16, 4
CA 64-17352c (1966)</div>

<u>Solvent effects on the spin resonance spectra of cobalt phthalocyanine</u>. (RCA Labs., Princeton, N.J.). J. Am. Chem. Soc. 87 (21), 4701-6 (1965) (Eng). A study of solvent effects on the electronic structure of the sq.-bonded Co^{2+} ion in the phthalocyanine mol. was carried out with several heterocyclic amines. One notable feature of the E.S.R. spectra is the superhyperfine structure arising from the magnetic interaction between the Co^{2+} unpaired electron and the out-of-plane solvating mols. A significant result found from these spectra is the sensitivity of the Co bonding parameters to the electronegativity of the solvent. A qual. comparison between the N-orbital bonding coeff. measured by E.S.R. and the calcd. charge d. at the N atom of the solvating mols. showed agreement.

Assour, J. M. and Harrison, S. E. 4
CA 62-12615f (1965)

Optical absorptions of phthalocyanines. (RCA Lab., Princeton, N.J.).
J. Am. Chem. Soc. 87 (3), 651-2 (1965)(Eng). The optical absorptions
and fluorescence spectra of the metal-free (H_2Pc) and Cu phthalocya-
nine (CuPc) complexes were measured. The λ_{max} in A., and (log ϵ) of
the absorption bands for H_2Pc in chloronaphthalene are 6990 (4.23),
6650 (4.19), 6450 (3.71), 6360 (3.71), 6170 (3.44), 6020 (3.54), 5760
(2.89), and 5550 (2.59). Addnl. bands (thin film of H_2Pc) were ob-
served at 3334 and 2892 A. Fluorescent bands for H_2Pc are found at
6990, 7350, and 7750 A. CuPc possesses absorption bands at λ_{max},
(log ϵ): 6780 (5.1), 6480 (4.36), 6110 (4.39), 5880 (3.57), 5640
(3.37), 4560 (2.38), 4270 (3.0), and 4140 (3.69). Other bands (thin
film of CuPc) were observed at 3292 and 2613 A.

Assour, J. M. and Kahn, Walter K. 4, 16
CA 62-6039f (1965)

Electron spin resonances of α- and β-cobalt phthalocyanine. (Polytech.
Inst. of Brooklyn, New York, N.Y.). J. Am. Chem. Soc. 87 (2), 207-12
(1965)(Eng). The magnetic properties of α- and β-Co phthalocyanine
polymorphs dild. metal-free, Zn, and Ni phthalocyanine were investi-
gated by E.S.R. The spectra of the 2 complexes reveal the difference
in their polymorphic structures. The Hamiltonian parameters, g fac-
tors, and hyperfine splitting consts. detd. from polycryst. samples
are compared with single-crystal work. The magnetic moment μ_{eff} =
2.38 Bohr magnetons obtained for α-Co phthalocyanine at room temp. is
15% lower than that in β-Co phthalocyanine. The ordering and sepn.
between the energy levels of Co^{2+} are discussed on the basis of the
exptl. data.

Badger, G. M.; Harris, R. L. N.; 1, 10, 2
Jones, R. A. and Sasse, Kenneth M. CA 58-433e (1963)

Porphyrins. I. Intramolecular hydrogen bonding in pyrromethenes and
porphyrins. (Univ. Adelaide). J. Chem. Soc. 1962, 4329-37. The NH
stretching frequencies in some porphyrins were compared with those of
related dipyrromethenes and dipyrromethanes. The effect of π-donor
solvents on the NH frequencies of some substituted pyrroles was also
studied.

Bandow, Fritz

13, 15
CA 48-9205 (1954)

Fluorescence of adsorbed dyes, especially of Acridine Orange on alumi-num oxide. (Max-Joseph-strasse 7, Mannheim, Ger.). Z. physik. Chem. (Frankfurt) [N.F.] 1, 63-8 (1954). The color of fluorescence of Acridine Orange (I) on Al_2O_3 greatly depends upon the H_2O contents of the used dye prepns. The assocd. complexes of I, the formation of which is favored by the presence of H_2O, show red emission color which changes into the green color of the nonassocd. single mols. or ions on drying, heating, and most easily on addn. of noneluting org. solvents (e.g. C_6H_6, MeOH, EtOH, Et_2O, Me_2CO, glycerol, paraffin oil, CCl_4, $CHCl_3$). The concn. of the dye on the adsorbent is not altered by this treatment. Similar observations were made with hematoporphyrin, quinine sulfate, thioflavine, trypaflavine, Rose Bengal, luminol, pyronine, 2,7-dimethyl-3-dimethylamino-6-aminoacridine, and chlorophyll.

Bannister, T. and Bernardini, J. E.

1, 15
CA 60-7068d (1964)

Physical and photochemical properties of a fluorescent chlorophyll colloid. (Univ. of Rochester, Rochester, N.Y.). Photochem. Photobiol. 2 (4), 535-49 (1963). A fluorescent colloid of chlorophyll a, prepd. in neutral phosphate buffer contg. 0.1-8.0% Tween 20 (polyoxyethylene sorbitan monostearate), was stable in the dark, had an absorption max. at 668 mμ. The colloid sensitized autoxidn. of p-toluenediamine which was independent of detergent and chlorophyll concns., but dependent on light intensity and substrate concn. Except for dependence on illumi-nation, the properties of the colloid were the same as those of dis-solved chlorophyll.

Bar, F.; Lang, H.; Schnabel, E.
and Kuhn, H.

2, 4, 15
CA 55-21793e (1961)

Direction of transition moments of absorption bands of phthalocyanines and porphyrins from fluorescence polarization measurements. (Univ. Marburg/Lahn, Ger.). Z. Elektrochem. 65, 346-54 (1961). An app. is described for the measurement of the degree of polarization, p, as a function of the frequency of the exciting radiation. Phthalocyanine (I) (metal-free and Mg complex), tetraphenylporphine (II) (free base, dihydrochloride, and Zn complex), and chlorophyll a (III) were examd. Free I shows 2 neighboring and partially overlapping absorption bands in the visible, each consisting of a main band and a series of minor bands spaced at 1500 cm^{-1} to higher ν.

Energy capture and conversion by photosynthesis. (Univ. of California, Berkeley). J. Theoret. Biol. 4, 52-72 (1963). Mechanisms of photosynthesis are discussed, particularly with respect to the transfer of electrons from O to C and other atoms. The process begins with the absorption of the energy of light by chlorophyll mols. with the formation of an excited state. The energy of the excited state is converted by an essentially solid state process to a charge sepn. between an electron and an electron hole. The electron eventually reduces diphosphopyridine nucleotide (TPN) making TPNH. The hole migrates through the pigment array, until it can oxidize a cytochrome mol. The oxidized cytochromes oxidize another coenzyme, and perhaps in the process produce adenosine triphosphate (ATP), this step being an enzymic reaction. The oxidized coenzyme must in turn get electrons from water, and since this reaction requires a large input of energy it must also use light absorbed by the pigment systems. This oxidn. of water requires Mn, perhaps in the form of a pigment. Also, the water-splitting reaction appears to utilize a different pigment system, and cannot be effected by absorption of light of wavelengths longer than 670 mμ. The transport of 4 electrons (liberating one O mol.) requires 6 or 8 photons, depending on the assumptions made, and produces 2 mols. of TPNH and 2 or more mols. of ATP. The overall efficiency for the production of these cofactors would not be as much as 50%, depending on the assumptions and based on the utilization of red (670 and 700 mμ) light. With shorter wavelengths the energy efficiency decreases in proportion to wavelength. The coenzymes (3 mols. of ATP and 2 of TPNH) are used with high efficiency (85%) to reduce CO_2 to carbohydrates and other products. ATP activates metabolites by increasing their energy content and making them more reactive towards carboxylation and redn. TPNH, which carries the larger part of the chem. potential from the light reactions, reduces a carboxyl C to an aldehyde C. The energy of the coenzymes not stored as chem. potential in the final products provides the driving force to make a complex series of reactions proceed at a rapid rate in the forward direction.

Becker, Ralph and Allison, Jean B.   2, 1

                                          CA 60-6357h (1964)

Metalloporphyrins. Electronic spectra and nature of perturbations. I.
Transition metal ion derivatives. (Univ. of Houston, Houston, Texas).
J. Phys. Chem. 67 (12), 2662-9 (1963). Low-temp. (77°K) emission spec-
tra are given for the following metal chelates of mesoporphyrin IX
dimethyl ester: Mn^{2+}, $Mn^{(3+)}$ acetate, Fe^{2+}, $Fe^{(3+)}$ acetate, Co^{2+},
$Co^{(3+)}$ chloride, VO^{2+}, Cu^{2+}, Ni^{2+}, and Pt^{2+}. Except for Cu, all the
emissions are phosphorescence, presumably arising from the triplet
state, and for which lifetimes (τ_p) are given (except for the triva-
lent state), as well as rough qual. intensities. In attempting to
account for differences in relative intensities and phosphorescence
lifetimes, consideration was given to the at. no. (Z), electronega-
tivity, and ionic and covalent size of the metal atoms. The absence
of fluorescence was considered to arise from a complete spin orbit
coupling involving the interaction of an at. triplet state with
porphyrin excited states. These states allow indirect coupling with
metalloporphyrin singlet and triplet states. In addn., another trip-
let state, intermediate to the normal porphyrin triplet and ground
states, and arising from a combination of the at. triplet and the
porphyrin ground state, was believed to play a role, e.g., in the dif-
ference in the quantum yield (ϕ) of phosphorescence (ϕ_p). In compar-
ing Zn and Ni, derivs., it was noted that although there was a large
diminution in fluorescence and phosphorescence, as well as a 7- to 8-
fold decrease in τ, of Ni, there was little or no change in Z, ionic
radius, or electronegativity. Were spin orbit coupling the sole fac-
tor responsible for the difference, this could explain the loss of
fluorescence, but ϕ_p should then be equal for both. The most feasible
explanation was presumed to be a new radiationless degradative mode in
the Ni compd. between the 1st excited singlet state, through a ligand
field and down to the ground state, plus a parallel mode in the triplet
manifold. Alternative explanations would have required information
concerning the geometry of the complexes, esp. the planarity of the
metal, and the p.d. of the metal orbitals of the complex. In compar-
ing the Cd, Pd, and Pt chelates with Ni, going from Ni to Pd increased
ϕ_p greatly and τ_p less so, while going from Pd to Pt gave very little
change in ϕ_p, but a large decrease in τ_p. The absence of fluorescence
and the high ϕ_p for both compds. was believed to indicate virtually
complete intercombination and little internal conversion. The small
diminution of ϕ_p for Pt compared with Pd was ascribed to a new or in-
creased rate const. for an internal conversion mode in the triplet mani-
fold. The large change in τ_p suggested that with a large change in Z,
though there may have been only little change in the coeff. of mixing
of excited states of different multiplicity, there was large change in
the degree of mixing of the triplet and ground states. In the transi-
tion metalloporphyrins, ϕ_p and τ_p were small. The preferred explana-
tion was that of a combination of the metal ion d states and the

porphyrin π states, the absence of fluorescence again being ascribed to virtually complete intercombination of excited states. The short lifetimes were then detd. by spin-orbit coupling with the strong, inhomogeneous field of the paramagnetic ion. II. Group II-A, II-B, and IV-A derivatives. Ibid. 2669-75. These studies were exte ded to the chelates of Mg, Ca, Zn, Sr, Cd, Sn, Ba, Hg, and Pb, although it was recognized that in many cases there was gross contamination by the free base porphyrin. Data were explained qual. as radiationless modes and (or) modification of the assocd. rate const., the latter arising from mol. distortion of changes in the ligand bonding scheme. Electronegativity and Z appeared to play a lesser role. III. Absorption spectra and solute-solvent interactions. Ibid. 2675-9. The soln. of Mg etioporphyrin II dissolved in pyridine, compared to 3-methylpentane, showed a splitting of the Soret band (the B transition). The addn. of stronger bases, such as NH_3 or triethylamine, resulted in the appearance of a new band at 640 mμ. The effect of pyridine was explained as the displacement of a mol. of water from coordination with Mg. The new band with the stronger bases was attributed to charge-transfer complex formation. Comparison of the Ba, Pb, and Hg mesoporphyrin di-Me ester IX compds. suggested that Ba should have a spectrum similar to that of Pb and Hg, since its size is even greater and should, therefore, be out of the plane even further. As its spectrum actually resembled that of the di-Na complex much more closely, it was suggested that electronegativity of the Ba was the controlling parameter, with the porphyrin having D_{4h} rather than C_{2v} symmetry.

Beinert, Helmut, Heinen, Wolfgang 　　　　1, 11, 16
and Palmer, Graham 　　　　　　　　　　CA 59-1899d (1963)

Applications of combined low temperature optical and electron paramagnetic resonance (EPR) spectroscopy to the study of oxidative enzymes. (Univ. of Wisconsin, Madison). Brookhaven Symp. Biol. 15 (BNL 738 (C-34)), 229-65 (1962). EPR spectra for submitochondrial particles, Cu complexes, Cu proteins, succinic coenzyme Q reductase, Nitrosomonas europaea, rat and beef heart, rat liver, reduced diphosphopyridine nucleotide dehydrogenase, bacterial prepns., hemerythrin, and Azotobacter particles were recorded at -170° to -178°. Optical reflectance spectra between 400 and 700 mμ were recorded at -90° using a modified Cary spectrophotometer. Interpretations of the spectra obtained are given along with the advantages and disadvantages of both methods.

Bellamy, W.

1, 3, 15
CA 58-9364h (1963)

Thermochemiluminescence of chlorophyll-carotene mixtures. (Gen. Elec.
Res. Lab., Schenectady, N.Y.). Nature 197, 482-4 (1963). Chemilumi-
nescence, with peaks at 695 and 745 mμ, has been observed on heating
in air varying mixts. of chlorophyll a and all-trans-β-carotene (I),
previously deposited from benzene solns. onto stainless steel disks.
Mixts. of I with pheophytin a, Zn tetraphenylporphine or the metal-
free base also exhibited chemiluminescence, but I and Cu tetraphenyl-
porphine failed to do so.

Bennett, J. E. and Ingram, D. J. E.

9, 16
CA 50-7583g (1956)

Analysis of crystalline hemoglobin derivatives by paramagnetic reso-
nance. (Univ. Southampton, Engl.). Nature 177, 275-6 (1956). Mea-
surements of single crystals of whale acid metmyoglobin were made at
20°K with a low-temp. resonator and at frequencies of 25,000 or 36,000
Mc. Angular variation was studied by rotating an electromagnet around
the resonator and plotting the field positions of the absorption line
against angle of rotation. The magnitude of the g value assocd. with
the single electronic transition varied from $g_{\perp}$ = 5.95 ± 0.05 to a $g_{\|}$ =
2.00 ± 0.01. For myoglobin of crystal type A, crystal symmetry $P2_1$,
the direction cosines for the axis through the Fe atom perpendicular
to the hem plane were 0.89, 0.36, and 0.28 for L, M, and N, resp. For
cryst. type B, crystals symmetry $P2_12_12_1$, the direction cosines were
0.13, 0.95, and 0.29 for L, M, and N, resp. An acid metmyoglobin
crystal immersed in a soln. of NaN_3 for a controlled time becomes half
azide deriv. and half acid metmyoglobin deriv. The g value of the
azide deriv. varies from $g_{\perp}$ of 2.8 ± 0.05 to $g_{\|}$ of 1.70 ± 0.05, with
distortion of axial symmetry. The occurrence of a single electronic
transition with g values spread across the free-spin value indicates
that the binding is of the d^2sp^3 type; this leaves one unpaired spin
with some orbital admixt.

Bennett, J. F. and Ingram, D. J. E. and
Gibson, J. F.

9,16
CA 51-15268b (1957)

Electron-resonance studies of hemoglobin derivatives. I. Hem-plane
orientation. (Univ. Southampton, Engl.). Proc. Roy. Soc. (London)
A240, 67-82 (1957). The application of electron-spin resonance to
the study of hemoglobin derivs. is outlined. Detailed information
can be obtained concerning the central iron atom and its immediate
surroundings. This information can be divided into two kinds, that
concerned with the electronic state of the iron atom and the type of

chem. binding, and secondly, that concerned with the symmetry of the iron atom's surroundings and thus the orientation of the hem planes. It is possible to det. the orientation of the hem planes with respect to each other and the crystal axes. Measurements for myoglobin and hemoglobin crystals are summarized. The latter show that the 4 hem groups per mol. are not parallel but that some have their normals along the direction of nearest approach to the neighboring mols.

Berezin, B. D.   2, 4, 13
CA 63-6380b (1965)

<u>Calculation of the relative equilibrium constants of reactions of formation of phthalocyanine (Pc) and porphyrin complexes from kinetic data.</u> (Chem.-Technol. Inst., Ivanovo). Zh. Fiz. Khim. 39 (5), 1082-6 (1965)(Russ); cf. CA 53, 16663i; 61, 6455f. In the same solvent and at the same temp., the ratio of equil. consts., K'/K'' of complexes of porphyrins, MX_2, is equiv. to the ratio of the rate consts. of their dissocn., k_1'/k_2' or $\Delta \log K = \Delta \log k$. This principle was applied to the equil. $H_2PC + MX_2 \rightleftharpoons MPc + 2HX$. The structural analogy of H_2Pc and HX justified the assumption that for them $\Delta \log k_2 \cong 0$. At 25° in H_2SO_4, using as a standard of comparison $K' = K_{ZnPcH^+}$, K_{H2SO4}, using as a standard of comparison $K' = K_{ZnPcH^+}$, $K_{H2SO4}.GaPcH^+$, or $K_{(H2SO4).SnPcH^+}$, the values of K'/K'' and of k_1 of the following were calcd.: $MPcH^+$, M = Mg, Zn, Co, Ni, Cu, Pd, and Pt; $H_2SO_4.MPcH^+$, M = Ga, Al, and Rh; and $(H_2SO_4)_2MPcH^+$, M = Sn, V, Os.

Bernard, H.   2, 11
CA 55-5627a (1961)

<u>Biosynthesis of the porphyrins.</u> (Acad. natl. méd., Paris). Pathol. et biol., Semaine hop. 7, 371-7 (1959); cf. CA 53, 20429a. A review with 19 references.

Bogorad, Lawrence   11,17
CA 55-4597a and e (1961)

<u>Biosynthesis of protochlorophyll.</u> (Univ. of Chicago). Ibid. 227-56. Proto-Comparative Biochemistry of Photoreactive Systems (V.1 of Symposia on Comparative Biology) Mary Belle Allen, ed., New York Academic Press, 1960.

Bolotnikova, T. N.

Spectroscopy of some simple aromatic hydrocarbons in frozen crystal-line solutions. Optika i Spektroskopiya 7, 217-22 (1959). Spectro-scopic measurements on naphthalene, anthracene, naphthacene, frozen in paraffin solvents, have shown that their bands are sufficiently sharp (having about 10-15 cm^{-1} band width) if the linear dimensions of the fluorescent mol. approx. coincide with the dimensions of the solvent mol. This is understood by assuming that the fluorescent mol. replaces the solvent mol. without a substantial distortion of its crystal lattice.

Botan, E. A.

Cytochrome c-cytochrome oxidase in bioluminescent fungi. (Avco Res. and Advanced Develop. Div., Wilmington, Mass.). Nature 198, 479 (1963). With the Nadi reaction as a presumptive test for the presence of cytochrome c- cytochrome c oxidase, a survey was made of 5 genera of bioluminescent fungi: Panus stypticus, Armillaria mellea, A. fusipes, Mycena polygramma, Clitocybe illudens, and Collybia velutipes. All organisms possessed the system, lending support to the hypothesis of McElroy and Seliger (Sci. Am. 207, No. 6, 76-91 (1962)) that bio-luminescence is a vestigial mechanism for the disposal of O by anaerobic organisms, a mechanism whose function was taken over by the later evolving cytochrome system.

Boucher, L. J., Crespi, H. L. and
Katz, J. J.

16641h Optical rotatory dispersion of phycocyanin. (Carnegie Inst. of Technol., Pittsburgh, Pa.). Biochemistry 5 (12), 3796-802 (1966) (Eng). The optical rotatory dispersion (ORD) (700-220 mμ) of phyco-cyanin isolated from the blue-green algae Phormidium luridum, Plecto-nema calothricoides, and Synechococcus lipidus was measured. ORD curves in the visible show multiple Cotton effects for the chromophore absorptions at $\sim$ 620 mμ (+) and $\sim$ 350 mμ (-). The uv ORD curves show a trough at 231 mμ with a crossover point at 222 mμ; the $[\alpha]_{231}$ of -3900 $\pm$ 200° indicates the protein to have a small amt. of α-helix conformation. Urea denaturation irreversibly destroys the optical activity of the chromophore absorptions. The ORD behavior of phyco-cyanins from P.luridum and Plectonema calothricoides resembles each other closely, while S. lividus phycocyanins are substantially dif-ferent. The ORD curves of pairs of protio- and deuterio-phycocyanins are essentially identical in both H_2O and D_2O. The rotatory disper-sion of phycocyanin appears to be independent of the state of aggrega-tion of the protein.

Brody, Marcia and Linschitz, Henry   15
                                                      CA 55-14546a (1961)

.Fluorescence of photosynthetic organisms at room and liquid nitrogen
temperatures. (Brandeis Univ., Waltham, Mass.). Science 133, 705-6
(1961). Fluorescence spectra were detd. at room and liquid N temps.
for Ochromonas danica, Chlorella pyrenoidosa, Euglena gracilis,
Porphyridium cruentum, Rhodospirillum rubrum, Rhodopseudomonas
palustris, Chromatium, and leaves of Prunus virginiana and Betula
papyrifera. In the algae and higher plants, fluorescence spectra
showed 2 bands, ascribed to monomer and aggregate forms of chlorophyll,
resp. At low temp., the long-wave-length emission was greatly enhanced
and often appeared as a new band. Photosynthetic bacteria, on the
other hand, showed no new bands at low temp., within the spectral
coverage and sensitivity of the measurements. A green fluorescence
was also found in algae; this is attributed to carotenoids.

Brody, S. S.   17, 15
                                                      CA 62-4366d (1965)

An estimate of the effective sizes of chlorophyll a aggregates in vivo
as determined from emission spectra. (Columbia Univ.). J. Theoret.
Biol. 7 (2), 352-9 (1964)(Eng). Low temp. fluorescence spectrum of
Euglena gracilis is observed to shift toward longer wavelengths dur-
ing the greening process. This shift is assumed to arise from the
formation of increasing larger aggregates of chlorophyll a. The
effective size and absorption max. are calcd. for the aggegate to be
3.8 mols. and 734 mμ, resp.

Brody, S. S. and Brody, M.   .   17, 15
                                                      CA 60-13575e (1964)

Aggregated chlorophyll in vivo. (Columbia Univ.). Natl. Acad. Sci.,
Natl. Res. Council, Misc. Publ. No. 1145, 455-78 (1963). Various
arguments are adduced to support the concept of polymeric forms of
chlorophyll (I) in soln., based on fluorescence and absorption spectra.
Thus, the fluorescence max. of in vivo systems at 685 mμ is ascribed
to the monomer, while that at 710 mμ is believed to be the dimer.
Changes in the fluorescence max. of aging algal cultures are inter-
preted as assocn. changes, the aggregated form being more fluorescent
than the monomer. A continuing red shift to 732 mμ in aging (80-hr.)
Euglena cultures is interpreted as a continuing aggregation of the I.
The av. aggregate at this fluorescence value is at least tetrameric.

Brody, S. S. and Brody, M.

Experiment showing that P700 can be an aggregated form of chlorophyll
a. (Columbia Univ.). Arch. Biochem. Biophys. 110 (3), 583-5 (1965)
(Eng); cf. Butler, CA 55, 21255h. If, with concd. solns. of chloro-
phyll (I) in which aggregation can occur, the 705 mμ band could not
be observed in the action spectrum for emission at 736 mμ, then it was
postulated that the possibility of a I aggregate giving rise to this
band in vivo could be eliminated. Measurements were made with chloro-
phyll a and with photosynthetic organisms; excitation spectra for
fluorescence at 736 mμ were detd. at 77°K with light-grown Euglena
gracilis strain Z and Chlorella pyrenoidosa. The excitation spectra
for Anacystis nidulans and Porphyridium cruentum were essentially
similar in the spectral region with which the study was concerned.
In each organism there was observed a band with max. at $\sim$ 705 mμ.
This band is a property of concd. solns. in EtOH; in dil. soln. it is
lacking. This study indicates that the spectral properties of P700
can be mainly attributed to aggregated I. It is suggested that P700
represents an assocn. of cytochrome with aggregated I, and it is con-
cluded that aggregated I has spectral properties similar to those of
P700.

Brody, S. S.; Newell, G. and
Castner, T.

Paramagnetic resonance of chlorophyll crystals and solutions. (Univ.
of Illinois, Urbana). J. Phys. Chem. 64, 554-7 (1960). A light-
induced resonance was observed both in chlorophyll crystals and solns.
The final product in the photoredn. of chlorophyll by ascorbic acid
in pyridine was not paramagnetic. The quantum yield of spin formation,
g-value, line width, and order of magnitude for the relaxation time
were given for crystals of chlorophyll a, chlorophyll b, and mixed
methyl chlorophyllide a and b, and chlorophyll in pyridine. The possi-
ble origins of the resonance were discussed.

Brody, Seymour and Brody, Marcia

Fluorescence properties of aggregated chlorophyll in vivo and in vitro.
(Columbia Univ.). Trans. Faraday Soc. 58, 416-28 (1962). The ratio of
fluorescence intensities at 77°K in EtOH at 720 and 685 mμ was consist-
ent with the assumption that a dimer was formed in concd. solns. The
fluorescence yield of the dimer was 0.8, the lifetime of emission from
this aggregated species corresponded to $\sim 10^{-4}$ sec. Fluorescence from
the chlorophyll monomer and aggregate, in vivo and in vitro, was

measured as a function of temp. (from 293-77°K). In soln. and in algae
the activation energy for dimer emission was approx. 1 kcal., the
Arrhenius const. was of the order of 10^4. The latter value reflected
a low transition probability for dimer emission, suggesting origin in
a triplet or nonbinding singlet state.

Brown, J. S.   17, 12
                                                           CA 61-965g (1964)

Forms of chlorophyll a and photosynthesis. (Carnegie Inst. of Wash-
ington, Stanford, Calif.). Colloq. Intern. Centre Natl. Rech. Sci.
(Paris) No. 119, 371-7, discussion 377-80 (1963)(in English). Chloro-
phyll a exists in vivo as distinct entities absorbing about 670 and
685 $m\mu$. Some plants contain a third form absorbing at 695 $m\mu$. Evi-
dence is presented that each of the major chlorophyll forms may medi-
ate each of the 2 light reactions now thought to be essential for
photosynthesis. Chlorophyll a_{695} may function in the same pigment
action as chlorophyll a_{670}, thereby extending the spectral range of
the light reaction.

Broyde, Suse B. and Brody, Seymour Steven   17, 11
                                                    CA 61-16348a (1964)

A new photochemical reaction of chlorophyll a. (Columbia Univ.).
Photochem. Photobiol. 3 (3), 265-7 (1964). When a soln. (8 x 10^{-4} M)
of chlorophyll a (I) in EtOH is illuminated with white light in the
presence of 2 x 10^{-1} M phenylhydrazine (II), I is transformed to a new
compd. with absorption max. at ~ 640 and 415 $m\mu$. After several hrs.
in the dark, I is regenerated as detd. by recovery of its absorption
at 662 $m\mu$, the extent of recovery being 50-70%. At very low concns.
of I (10^{-6} M) only slight fading of I occurs on irradiation. The spec-
tral data are suggestive of I-II interaction at the cyclopentanone
ring V of I.

Broyde, S. B. and Brody, S. S.   17, 1
                                                     CA 63-4569c (1965)

F-698—pigment found in preparations of chlorophyll. (Columbia Univ.).
Biochem. Biophys. Res. Commun. 19 (4), 444-51 (1965)(Eng). F-698 has
a fluorescence max. at 698 $m\mu$ in Me_2CO at 77°K. F-698 is present in
the chlorophyll b fraction, and in some samples of chlorophyll a_1 which
were prepd. from young spinach. Rechromatographing the chlorophylls
several times results in prepns. free of F-698. The presence of
F-698 is revealed at room temp. by difference spectroscopy. At room
temp. the absorption max. are approx. 415 and 675 $m\mu$. At -80° the red

absorption band of F-698 can be resolved in optically dense solns. of chlorophyll b without resorting to difference spectroscopy; the max. being 688 mμ. F-698 is not a chlorophyll colloid, as colloids of chlorophyll a shift in their absorption max. on cooling to -80°.

Brucker, Wolfgang and Nicolau, Claude   16, 17
CA 55-15639 (1961)

Electron-spin resonance determination in photosynthesis of green plants. (Inst. Med. Biol., Berlin-Buch). Naturwissenschaften 47, 89-90 (1960). Electron-spin resonance (ESR) measurements of photosynthesis in barley leaves suggested that the oxidn. of cytochrome and redn. of the pyridine nucleotides involved may be the 1st steps of this photosynthesis. In investigations on catalytically active compds., riboflavine, diphosphopyridine nucleotide, and adenosine triphosphate and its complexes showed ESR signals with different electron donors.

Brugger, J. E.   15, 17
CA 52-10303c (1958)

Fluorescence yield of chlorophyll in Chlorella as a function of light intensity. (Univ. of Chicago). 113-17. Discussion.

Butler, W. L. and Bishop, N. I.   1, 17, 15
CA 60-16216d (1964)

Action of two-pigment system on fluorescence yield of chlorophyll a. (U.S. Dept. of Agr., Beltsville, Md.). Natl. Acad. Sci., Natl. Res. Council, Misc. Publ. No. 1145, 91-100 (1963); cf. Duysens, CA 58, 14444b. Green-bean leaves, spinach chloroplasts, and suspensions of Scenedesmus were irradiated by actinic light and absorption spectra measured at -196°. The action spectra of green leaf was similar to that of Chlorella (Myers and Graham, CA 58, 10499c). The absorption spectra of Scenedesmus showed that the same amts. of chlorophyll b, chlorophyll a$_{760}$ and chlorophyll a$_{680}$ were present in all samples. The mutants carried a normal complement of pigments in systems 1 and 2. CO_2 mutants failed to fix CO_2 in the light but evolved O in a Hill reaction. O mutants failed to evolve O in the light but photoreduced CO_2 in H atm. P was present in the wild-type cells and in the O mutant but not in CO_2 mutant.

Butler, W. L. and Norris, K. H.   17, 15
                                                    CA 58-7073d (1963)

Lifetime of the long-wavelength chlorophyll fluorescence. (Agr.
Marketing Ser., Beltsville, Md.). Biochim. Biophys. Acta 66, 72-7
(1963)(in English). The fluorescence lifetime of chlorophyll in vivo
and in vitro was measured with a phase fluorimeter. The lifetime in
vivo of the long-wavelength emission (730 mμ) which appears at low
temp. was 3.1 mμ sec. It is concluded that this emission is fluores-
cence rather than phosphorescence as had been previously reported.

Butler, Warren L.   1, 10
                                                    Optical Soc. of Amer.
                                                    52 (1962) 292-9

The transmission and absorption properties of turbid media have been
examined with Kubelka and Munk's theory of the optics of intensity
scattering material. The equation for the optical density of such
material as a function of thickness has been derived and examined
experimentally. It is shown that the reflectivity and scattering
coefficient can be determined absolutely without reference to a stand-
ard material from the optical-density measurements. The absorption
spectra of pigments in scattering media and in clear solution have
been compared. It is shown that light in passing through a turbid
sample may traverse an optical path which is many times the sample
thickness. The practical consequence of this increased path length
is an intensification of the absorption bands of pigments in light-
scattering media. The theoretical expression for this intensification
has been derived and tested experimentally. Spectral effects due to
the physical binding of pigment molecules to the scattering particles
have also been examined.

Butler, Warren L. and Norris, Karl H.   1, 5
                                                    CA 54-13243e (1960)

The spectrophotometry of dense light-scattering material. (U.S. Dept.
of Agr., Beltsville, Md.). Arch. Biochem. Biophys. 87, 31-40 (1960).
The use of an app. (monochromator and photometer) is described. The
optical path length of a light-scattering sample may be many times the
sample depth. By adding $CaCO_3$ to reduced cytochrome c solns., the in-
tensity of the absorption bands was intensified 70-fold as a result of
a 70-fold increase in path length. Data are given on a similar in-
tensification (over 10-fold) in the spectrum of solid apple tissue in
which various forms of chlorophyll and other pigments are involved.
The photoreversible pigment which controls many developmental responses
of plants was demonstrated spectrophotometrically in intact corn

coleoptiles. Cytochrome, various forms of chlorophyll, and carotene are also involved in the spectra of lima bean seeds, which change in the process of germination. The spectra of dry yeast (com. bakers' yeast) are presented in comparison with yeast suspensions. In addn. to the typical cytochrome component, there is a cyanide-sensitive absorption band at 640 mμ. By use of the app., the efficiency of a pigment extn. can be detd. on the extn. residue, revealing pigment bound to the residue in a non-extractable form. 22 references.

Butler, W. and Baker, J. E.   1, 17
                                                         CA 58-10865f (1963)

Low-temperature spectra of chloroplast fragments. (Agr. Marketing Ser., Beltsville, Md.). Biochim. Biophys. Acta 66, 206-11 (1963) (in English). Absorption and fluorescence excitation spectra of chloroplast fragments, obtained by sonic oscillation and differential centrifugation, were measured at -196°. Several chlorophyll pigments, including C-705, were resolved in the low-temp. spectra. No fractionation of the chlorophyll pigments was achieved by differential centrifugation. The smallest chloroplast fragments (those in the supernatant of a 173,000-g centrifugation) contained the chlorophyll pigments in the same ratio as the intact chloroplasts. The fluorescence excitation spectra showed that energy transfer between the pigments assocd. with the smallest fragments occurred to the same degree as in the intact chloroplasts. These results support the concept of a structural photosynthetic unit in which a C-705 mol. serves as an energy sink.

Butler, W. L.   1, 17
                                                         CA 55-21255h (1961)

A far-red absorbing form of chlorophyll in vivo. (U.S. Dept. of Agr., Beltsville, Md.). Arch. Biochem. Biophys. 93, 413-22 (1961). Fluorescence excitation spectra and absorption spectra of leaves at -196° reveal a 705-mμ absorbing component which fluoresces at 720 mμ. Resonance transfer of energy from chlorophyll a to the long wave length component -196° is shown by the sensitization of the 720-mμ fluorescence by chlorophyll a and the photosynthetic accessory pigments. Energy transfer to the 705-mμ absorbing component at room temp. is indicated by data on the fluorescence quenching of chlorophyll a at room temp. It is proposed that the 705-mμ absorption band is due to a complex of cytochrome and chlorophyll a.

Butler, Warren L.

Effects of red and far-red light on the fluorescence yield of chloro-
phyll in vivo. (U.S. Dept. of Agr., Beltsville, Md.). Biochem. Bio-
phys. Acta 64, 309-17 (1962)(in English). Evidence is given for the
participation of chlorophyll C-705 in the photochemistry of photo-
synthesis. The fluorescence of chlorophyll a and C-705 in green leaves
was examd. during the induction period of photosynthesis in air and N.
Brief illumination of a leaf with red light caused an increased yield
of chlorophyll a fluorescence, which lasted longer in N than in air.
This increased yield was inhibited by subsequent irradiation with far-
red light. The action spectrum for the effect of far-red light showed
a max. near 705 mμ. It is considered that the effects of red and far-
red light on the fluorescence yield of chlorophyll a are a manifesta-
tion of the 2nd Emerson effect.

Bystrova, M. I. and Krasnovskii, A. A.

Fluorescence spectra of protochlorophyll and protopheophytin in dif-
ferent states. (A. N. Bakh Biochem. Inst., Moscow). Biofizika 10 (3)
433-40 (1965)(Russ); cf. CA 54, 21356e; 58, 10440h. Protochlorophyll
(I) extd. from squash seeds and chromatographed, and pheoprotochloro-
phyll (II), prepd. from I by acidification in Et_2O soln., were sub-
jected to fluorescence spectrometry. In general, 2 peaks appear, 1
below 680 mμ and 1 above. Solns. of I and II show longest λ fluores-
cence in polar solvents. One or both peaks for either I or II split
at $-196°$ compared with $20°$ in alc. and in pyridine. Adsorbates of
I or II on filter paper or powdered cellulose show displacement of λ
at both peaks and a change of relative intensity of the 2 peaks com-
pared with solns. The adsorbate spectra depends on concn., temp.,
water content of the solvent during prepn., and rate of evapn. of
solvent. Addn. of water to adsorbates of II, but not of I, caused a
shift in spectra to longer λ and appearance of an addnl. ir peak.
Solid films, prepd. by evapn. of Et_2O solns., show a diffuse fluores-
cence, with peaks at 700 and 760 for I and 685 and 760 mμ for II. For
I, fluorescence is observed only at low temp. Active I in vivo has
the greatest similarity in fluorescence to II in pyridine soln. and
in adsorbates. Spectra of adsorbates of I resemble inactive I in vivo.

Bystrova, M. I., Umrikhina, A. V. and   15, 17
Krasnovskii, A. A.   CA 64-13016d (1966)

Photoreduction of protochlorophyll and protopheophytin. (A. N. Bakh
Inst. Biochem., Moscow). Biokhimiya 31 (1), 83-92 (1966)(Russ).
Protochlorophyll (I) from pumpkin seeds showed max. absorption at 455
and 430 mμ. Photopheophytin (II) was obtained by treatment of I in
Et ether with 10% HCl, shaking, and washing with water to remove
acidity. Photoredn. was carried out in vacuo. Redn. of I with
ascorbic acid, phenylhydrazine, and reduced benzylnicotinamide produced
a compd. with absorption max. at 470 mμ, apparently as a result of
redn. of the conjugated double bond system of I. Redn. of I and II
with Zn amalgam in the dark resulted in by-products with max. absorp-
tion at 470 and 525 mμ. Solns. of I and II in pyridine revealed an
irreversible reaction of the pigments with amine, producing fission
of the cyclopentanone ring with characteristic spectral changes. The
deriv. of II in alc. pyridine sol. at -40° produced a compd. with
absorption max. at 640 mμ.

Calvin, Melvin   17, 13
                                                         CA 55-13485e (1961)

Some photochemical and photophysical reactions of chlorophyll and its
relatives. (Univ. of California, Berkeley). Ibid. 317-55. IN: Sym-
posium on Light and Life, Johns Hopkins University, 1960,Light and
Life; proceedings. Edited by William D. McElroy and Bentley Glass.
(Johns Hopkins University. McCollum-Pratt Institute. Contribution
No. 302).

Cederstrand, Carl N., Rabinowitch, Eugene   1, 15, 17
and Govindjee   CA 65-4260c (1966)

Absorption and fluorescence spectra of spinach chloroplast fractions
obtained by solvent extraction. (Univ. of Illionis, Urbana). Biochim.
Biophys. Acta 120 (2), 247-58 (1966)(Eng). Chlorophyll components
were sepd. in vivo by fractional extn. of chloroplasts with Me_2CO and
MeOH of various concn. Dil. solvents were found to ext. more or less
intact chlorophyll-carrier complexes. More concd. solvents dissocd.
these complexes, in the exts., and in the residual chloroplast mate-
rial. The absorption and fluorescence spectra of the exts. and the
residues suggested a partial sepn. of two types of complexes, with the
"long-wave" component, chlorophyll a 683, extd. ahead of the "short-
wave" component, chlorophyll a 668. At -196° all chlorophyll a com-
plexes became fluorescent, while only one fluoresced strongly at room
temp. The relative intensities of the fluorescence max. at 685 mμ,
696-700 mμ, and 735 mμ change with solvent concn.

Chadderton, Lewis T.

Optical properties of the phthalocyanines. (Cavendish Lab., Cambridge, Engl.). J. Phys. Chem. Solids 24 (6), 751-7 (1963). If the spectral shifts arising from temp. dependence and the broadening due to crystal field effects are accounted for there is a 1:1 correspondence between peaks observed in vapor, sublimed film, and single-crystal absorption spectra. The simple band model offers a reasonably good description of cryst. Cu, Pt, and metal-free phthalocyanines. The sharp energy levels of the free mol. transform into broad quasicontinuous bands on crystn.

Chiorboli, Paolo; Rastelli, Augusto and
Momicchioli, Fabio

Theoretical studies in the chemistry and physics of heterocycles. I. The π-electron system and uv spectrum of pyrrole. (Univ. Modena, Italy). Theoret. Chim. Acta 5 (1), 1-10 (1966)(Eng). L.C.A.O.-S.C.F. calcns. with 4 different sets of parameters are given for the π-electron structure of pyrrole. The aim was mainly to discuss whether such calcns could account for the mol. properties, or the σ system ought to be explicitly included. The effects of different values for the integrals were discussed by comparing final results, concerning both the ground state and the excited states. A good agreement with exptl. data was obtained. The usual limited configuration mixing on these S.C.F. results, leading to a poor agreement for the energies as well as to a lack of qual. sequence of intensities, does not allow a clear interpretation of the uv spectrum.

Cho, F., Spencer, J. and Govindjee   1, 15

Emission Spectra of Chlorella at Very Low Temperatures (-269° to -196°), Biochim. Biophys. Acta, 126, 174 (1966)

Cho, F., and Govindjee   1, 15

Fluorescence Characteristics of Chlorella at Low Temperatures (4°K to 77°K). Abstract only.

Clar, Erich

Polycyclic Hydrocarbons - New York, Academic Press, 1964, 2 vols.

Clayton, R. K.   12, 13
                                                        CA 59-1963d (1963)

Primary reactions in bacterial photosynthesis. II. The quantum
requirement for bacteriochlorophyll conversion in the chromatophore.
(Oak Ridge Natl. Lab., Oak Ridge, Tenn.). Photochem. Photobiol. 1,
305-11 (1962); cf. CA 58, 2672d. The extinction coeff. of bacterio-
chlorophyll (I) at its long-wave max. is calcd. roughly to be 7.3 x
10^7 at a d. of 1 mole/cm^2; this figure is used also for the special
component, denoted (II), of I. A quantum requirement necessary for
the reversible alteration, involving bleaching of the long-wave
absorbtion band at 870-90 m_μ and a blue shift of the 800 m_μ band, of
one mol. of II is estd. to be from 2 to 4 quanta, even in dry prepns.
at 1^oK. The conclusion is reached that II is an effective sink for
excitation energy in the chromatophore.

Clayton, Roderick K.   1, 12, 17

Absorption Spectra of Photosynthetic Bacteria and their Chlorophylls.
Bacterial Photosynthesis - Howard Gest, Anthony San Pietro and Leo P.
Vernon (ed.).

Clayton, Roderick K.   13, 15
                                                        CA 66-8931f (1966)

Relations between photochemistry and fluorescence in cells and extracts
of photosynthetic bacteria. (Charles F. Kettering Res. Lab., Yellow
Springs, Ohio). Photochem Photobiol. 5 (10), 807-21 (1966)(Eng); cf.
Vredenberg and Duysens, CA 58, 8249g. Under aerobic conditions light-
induced changes in the fluorescence yield showed a strict correspond-
ence with the bleaching of the specialized reversibly-bleached bacteri-
ochlorophyll P 870 in Rhodospirillum rubrum, Chromatium and Rhodo-
pseudomonas spheroides. This was not observed under anaerobic condi-
tions. Redn. of a primary photochem. electron acceptor might be
involved. In chromatophore prepns., changes in rate consts. for
quenching of singlet excitation energy occurred. A band shift of
bacteriochlorophyll also occurred. These effects were absent under
aerobic conditions.

Clayton, R. K.   1, 3, 5, 13
                                                  CA 59-1963e (1963)

Reactions of carotenoids and cytochromes in illuminated bacterial
chromatophores. Ibid. 313-23. The light-induced bleaching and red
shift of the absorption bands reaction of carotenoids is eliminated
immediately and irreversibly by exposure to deoxycholate. The reac-
tion is greatest in wet chromatophores; exhaustive desiccation elimi-
nates reversibly all the light-induced optical changes. In dry films,
the reaction is present appreciably only at an optimum, very low H_2O
vapor concn. The carotenoid reaction has the following attributes:
It occurs reversibly in air-dried material at 1^OK, showing approx. the
same decay kinetics as the reversible change of II; reversible trap-
ping of electrons or holes at room temp., but at not less than 150^OK,
is suggested by decay kinetics; extreme sensitivity to structural
alterations; in some instances, the onset of the reaction lags behind
that of other reactions. These are interpreted as arising from the
diffusion of electrons or holes from the area of II to the carotenoid
mols., altering their absorption spectra. In Chromatium, the bleach-
ing at 423 $m\mu$ is due to a light-induced cytochrome oxidn., appearing
to be closely connected to the II alteration. The data indicate that
electron vacancies arising in II are transferred rapidly to the
cytochrome.

Clayton, Roderick K.   12
                                                  CA 63-7363a (1965)

Molecular Physics in Photosynthesis (A Blaisdell Book in the Pure and
Applied Sciences). New York: Blaisdell. 1965. 205 pp.

Clezy, P. S. and Morell, D. B.   1, 9

A spectroscopic study of haematin compounds in the Soret region.
Biochimica et Biophysica Acta, 71 (1963) p. 165-171.

Clezy, P. S. and Nichol, A. W.   7, 13
                                                  CA 64-8185b (1966)

Chemistry of pyrrolic compounds. I. Synthesis of oxoporphyrins.
(Univ. New South Wales, Kensington). Australian J. Chem. 18 (11),
1835-45 (1965) (Eng).

Condacse, A. and Radulescu Em.   2, 13, 11
                                                        CA 63-16631d (1965)

Biosynthesis and physiology of porphyrins. (Serviciul Med., Spitalul
Ministerului Finantelor, Bucharest, Rom.). Med. Interna 17 (6), 669-
74 (1965)(Rom). A review of 24 references.

Csuri, I. J.   13, 1
                                                        CA 64-16844c (1966)

Ultraviolet and visible spectroscopical examinations of diachrome and
fluorochrome dyes. (Univ. Med. School, Budapest, Hung.). Acta
Histochem. 22 (5-8), 283-97 (1965)(Eng). In histochem. reactions the
formed or reacted dye often undergoes unexpected changes. The rela-
tion between structure and spectroscopic properties of several dyes
was studied. The uv spectra of aq. dye solns. at different concns.
were detd. 3-Dimensional spatial figures were prepd. because they
best depicted changes occurring during diln. The figures demonstrate
the % transmission, the dilns., and the wavelengths. The dyes were
grouped as follows: phthalocyanine group (Alcian Blue (I)); thiazine
group (Azure A (II)); acridine group of xanthene dyes (Acridine Orange
(III), Acridine Yellow (IV), Aurophosphine (V)); rhodamine group of
xanthene dyes (eosine (VI), fluorescein (VII)); triphenylmethane group
(Aniline Blue (VIII)); nitroso group (Naphthol Green (IX)); thiazole
group (primuline (X)); and disazo group of azo dyes (Congo red (XI)).
From the spectra, the 11 dyes are arranged into 3 classes; regular
spatial spectra, medium perturbed spatial spectra, and strongly per-
turbed spatial spectra. A regular spatial figure is found in VIII,
IX, III, I, and II. The spatial figures of IV, X, and V show a medium
perturbation. In IV, this appears at 4800-5100 A. In X, perturbation
of the spatial figure also falls between 4050 and 5100 A., but a few
dilns. show irregularities also between 6250 and 6750 A. Among the 3
dyes, the spatial figure of V is the most irregular, in which perturba-
tions occur, 4800-5780 A. In aq. medium, assocn. between the mols. of
X occurs, 3360-4800 A., whereas dissocn. appears at 5100 A. Irregu-
larity is complete at 4800 A. These observations correspond to the
perturbation points to be found on the spatial figure. A strongly
perturbed spatial figure was obtained in the spectra of VI, VII, and
XI. Perturbation of VI lies at 5400-5780 A. VII showed the greatest
perturbation, 4800-5100 A. The most tangled spatial figure was due to
XI, from 5400 A. toward greater wavelengths. Perturbation of the
spatial figures occurred more often at certain wavelengths. Its occur-
rence was 40% at 4800-5100 A., 15% at 5780 A., and 11% at 4050-4360 A.

Dadykin, V., Chernomorskii, S. A.   1, 17, 3, 11
and Potaevich, E. V.   CA 61-6085e (1964)

Correlation between the absorption of radiant energy and the pigment content in suspensions of Chlorella. (Karelian Branch Acad. Sci. U.S.S.R., Petrozavodsk). Botan. Zh. 49 (3), 398-403 (1964). The contents of chlorophylls and carotenoids and light absorption curves were detd. in 12 mutants of Chlorella. Differences in absorption of light are connected not only with various amts. of cell pigments but also with their compn., formation of lipoprotein complexes, and the presence of intermediary metabolites. 17 references.

Dahl, J. P. and Hansen, Aage E.   7, 10
    CA 59-115h (1963)

Self-consistent field molecular orbital calculation for pyrrole. (Univ. Copenhagen). Theoret. Chim. Acta 1, 199-205 (1963) (in English). The electronic structure and spectrum of pyrrole were studied by using the semiempirical L.C.A.O.-S.C.F.-M.O. method. With configuration interaction included, low excited singlet states were calcd. to occur at 5.98, 6.74, 7.33, and 8.20 e.v., in good agreement with exptl. values of about 5.88, 6.77, and 7.21 e.v. The dipole moment of the mol. was calcd. to be 1.84D, as compared with the exptl. value, 1.80D. Tables of spherical-core-attraction integrals for combinations of C and N atoms are presented.

Dhere, Ch. and Bois, Elphege   2, 15, 11
    CA 21-109 (1926)

Fluorescence of natural and artificial porphyrins. Compt. rend. 183, 321-3 (1926); cf. C.A. 18, 3141; 19, 936. The spectra of the fluorescence of the natural products protoporphyrin, uroporphyrin and coproporphyrin, and of the artificial products hematoporphyrin, mesoporphyrin, etioporphyrin and isoetioporphyrin in 1 in 50,000 soln. in pyridine are tabulated.

New method for the production of heraphathite. A. Zimmern. Compt. rend. 182, 1082-3 (1926). Herapath prepd. herapathite by mixing with heat an alc. soln. of I with an aceto-alc. soln. of neutral quinine sulfate. (Cf. Phil. Mag. 3, 161; 4, 346 (1852-53)). The crystals obtained were too small for optical use. The new method substitutes vapor of I at definite temp. in place of the tincture of I, and yields plates 2 or 3 cm on a side.

Djuric, D.   2, 15
                                                    CA 56-3750

Fluorescence of porphyrins. Arhiv Farm (Belgrade) 11, 1-6 (1961).
A review with 46 references. (Not in English.)

Duysens, L. N. M., Amesz, J.   1, 12, 17, 15
and Kamp, B. M.   CA 55-21247h (1961)

Two photochemical systems in photosynthesis. (State Univ., Leiden,
Neth.). Nature 190, 510-11 (1961). Evidence is summarized for the
postulate that two pigment systems (I and II) are necessary for opti-
mal photosynthesis. System II, with max. activity at 560 mμ (in
Porphyridium cruentum) includes the fluorescent chlorophyll a and
most of the phycobilins (primarily phycoerythrin). It is responsible
for the action spectrum of chlorophyll a fluorescence and on illumina-
tion reduces the cytochrome (f or c) band at 420 mμ. System II (with
max. activity at 680 mμ) includes the non- or weakly-fluorescent
chlorophyll a and some phycobilins. On illumination it reduces the
420 mμ cytochrome (f or c) band. For equal incident quanta, the ratio
of activity at 570 to 680 mμ is 83.5/20.6. The algae show an Emerson
effect, i.e., if illuminated at both wavelengths, the rate of photo-
synthesis is higher than the sum of individual rates. A scheme of
the function of systems I and II is presented and is believed to be
applicable to photosynthesis of higher and lower plants.

Eastwood, D., Edwards, L.   4, 10 , 15
and Gouterman, M. and Steinfeld, J.   CA 66-15418d (1966)

Spectra of porphyrins. VII. Vapor absorption and emission of
phthalocyanines. (Harvard Univ.). J. Mol. Spectrosc. 20 (4), 381-90
(1966) (Eng); cf. CA 65, 16075a. Absorption spectra and fluorescence
spectra excited by the He-Ne laser line at 633 mμ are reported for
H_2Pc, MgPc, and ZnPc in the vapor. CuPc showed no vapor emission.
The yields of fluorescence are temp. dependent, but relatively inde-
pendent of the presence of the foreign gases Ar, N, CF_2Cl_2. There is
no evidence for resonance fluorescence. The implication of the observa-
tions for the theory of radiationless transitions is discussed.
24 references.

Eberhardt, W. H. and Renner, H.   18
                                                   CA 55-19470i (1961)

The magnetic rotation spectrum of singlet-triplet transitions,
(Georgia Inst. of Technol., Atlanta). J. Mol. Spectroscopy 6, 483-91
(1961); cf. CA 55, 10054c. The magnetic rotation spectra were ob-
served for several substances in regions thought to correspond to
singlet-triplet transitions. The magnetic rotation spectrum of HCHO
in the region 3700-3960 A corresponded to the absorption spectrum.
For glyoxal, the spectrum was very intense, and the band structure had
a peculiar appearance. Acrolein had an extremely weak band at 4123 A.
Benzoquinone exhibited 1 band at 5352.2 A which was apparently a
superposition of many lines shaded to the red. No rotation spectra
were observed for these compds.: AcH, biacetyl, crotonaldehyde,
$C_{10}H_8$, $1-BrC_{10}H_7$, 1, 4-naphthoquinone, and fluorene. The observed
spectra are discussed in detail. The magnetic rotation spectral tech-
nique appeared quite useful for the identification and characteriza-
tion of singlet-triplet transitions.

Efremova, R. V.   1, 17
                                                   CA 54-22001d (1960)

Aggregation of chlorophyll and chlorophyllide molecules. Izvest. Akad.
Nauk S.S.S.R., Ser. Fiz. 24, 616-19 (1960). Absorption and luminescence
spectra were obtained of chlorophyll a and of chlorophyllide in concns.
10^{-3}-10^{-7} mole/l. in H_2O, EtOH, and in binary mixts. EtOH and H_2O.
H_2O in EtOH causes aggregation of chlorophyll which can be reversed by
a rise in temp. to 40°. Chlorophyllide is present in 2 states:
monomeric (max. 630 mµ) and dimeric (max. 652 mµ). The purely mono-
meric form of chlorophyllide is present only at 10^{-6}-10^{-7} mole/l.
Increase in temp. dissoc. the dimer.

Egle, Karl   11, 17
                                                   CA 48-8877 (1954)

Biosynthesis of chlorophyll pigments. (Univ. Frankfort, Ger.).
Naturwissenschaften 40, 569-76 (1953). A review on synthesis of
chlorophyll in the plant, protochlorophyll, basic building blocks for
porphyrins, and the phyllogeny of pyrrole pigments. Many references.

Elliott, W. B. and Doebbler, G. F.   1, 13
                                            CA 65-2600b (1966)

Problems in low-temperature spectrophotometry of turbid specimens.
(State Univ. New York, Buffalo). Anal. Biochem. 15 (3), 463-9 (1966)
(Eng). Depression of the Soret absorption peak of reduced cytochrome
c is partially caused by multiple reflection of forward scattered
light, causing it to reach the photomultiplier without passing through
the specimen. A simple insert for the Dewar which reduces multiple
reflection of forward scattered light is described. A change in the
ratio of Soret to α absorbance of reduced cytochrome c is observed on
cooling to -196°.

Evstigneev, V. B.   1, 13, 17
                                            CA 47-3903c (1953)

Effect of solvent on the absorption spectra of chlorophyll. (Bakh
Biochem. Inst., Moscow). Biokhimiya 17, 559-62 (1952). The results
of Harris and Zscheile (C.A. 37, 4628[8]) are subjected to a crit. anal-
ysis. The change in absorption at the same concn. of chlorophyll is
slight when the solvent Et_2O is replaced by Me_2CO. Thus, the max.
absorption in the red for the Et_2O soln. is 660 mμ, and the extinction
coeff. 0.472. The corresponding values for the Me_2CO soln. are 662 mμ
and 0.431. The max. absorption in the blue for the Et_2O soln. is 428
mμ, and the extinction coeff. 0.625. For the Me_2CO soln. the corre-
sponding values are 430 mμ and 0.542. The absorption spectra of
chlorophyll in different solvents published by H. and Z. are not com-
pletely comparable and their use for analytical purposes can lead to
errors.

Evstigneev, V. and Bekasova, O. D.   17, 13
                                            CA 60-13500a (1964)

Photoreduction of chlorophyll a, bacterioviridin, bacteriochlorophyll,
and protochlorophyll in nonpolar solvents. (A. N. Bakh Biochem. Inst.,
Moscow). Dokl. Akad. Nauk SSSR 154 (4), 946-9 (1964). Chlorophyll a
during photoredn. at room temp. or -45° in MePh gave a new absorption
max. at 585 mμ. The reaction was reversed in the dark but was slow,
being accelerated by O and elevation of the temp. Polar solvents
repressed the formation of the new 585 mμ max. The photoredn. of
bacterioviridin under these conditions was slower than that of
chlorophyll a, but the reduced soln. had maxima at 510 and 560 mμ;
the reverse reaction in the dark was very slow. Pyridine accelerated
the reaction and suppressed the 560 mμ max.; the acceleration was
greater for the reverse dark reaction. Bacteriochlorophyll after

photoredn. was nearly colorless, while photochlorophyll reduced to a product with one max. at 470 mµ. Pyridine accelerated the direct reaction but had little effect on the slow reverse, dark reaction. It also produced a weak max. at 665-70 mµ. The photoredn. was accomplished with PhNHNH$_2$.

Evstigeneev, V. B. and Gavrilova, V. A.   1, 11, 17
                                                       CA 55-10516e (1961)

The ability of adsorbed chlorophyll to photosensitize oxidation-reduction reactions. Biofizika 5, 599-608 (1960). Chlorophyll a and b, protochlorophyll, pheophytin, phthalocyanin-Mg and -Cu were adsorbed from MeOH, EtOH, Et$_2$O, dioxane, acetone, etc. on Al$_2$O$_3$, ZnO, Ca$_3$(PO$_4$)$_2$, hemoglobin, SiO$_2$, 30 v. 400 w. lamp with a condenser and filters while suspended in solns. of electron donors and acceptors, e.g. ascorbic acid + methyl red. The I/I$_0$ of the acidic mixt. at 520 mµ was plotted against time. The reaction rate was proportional to the vol. concn. of the adsorbate and to the light intensity, and increased with the surface area of the adsorbate, and the temp. The red max. of chlorophyll appeared flattened and shifted to 665-80 mµ. Theophytin Cu in org. soln. or adsorbed on ZnO was inert toward PhN$_2$,H$_3$ or ascorbic acid, but was active on Al$_2$O$_3$. Short-lived semiquinone ion-radicals initiate the reactions by electron withdrawal.

Falk, J. E., Appleby, C. A.   9, 11, 2
and Porra, R. J.

The Nature, Function and Biosynthesis of the Haem Compounds and Porphyrins of Legume Root Nodules. Symposium Society Experimental Biology, 13 (1959) p. 73.

Falk, J. E.   9

Some New Compounds of Haems with Bases. Haematin Enzymes, Vol. 19, Part 1 (1959) p. 74-76, Pergamon Press.

Falk, J. E. and Perrin, D. D.   2, 9, 13

Spectra and Redox Potentials of Metalloporphyrins and Haemoproteins. Haematin Enzymes, Volume 19 (1959) p. 56-79, Pergamon Press.

Falk, J. E.   1-17

Spectra and Appendix Tables.   Porphyrins and Metalloporphyrins - Vol. 2.

Falk, J. E. and Nyholm, R. S.   13

Current Trends in Heterocyclic Chemistry, Butterworths, London (1958),
p. 130, edited by Albert, A., Badger, G. M. and Shoppee, C. W.

Falk, J. E. and Perrin, D. D.   9

Haematin Enzymes, Pergamon, London 1961, p. 56.   Falk, J. E., Lemberg,
R. and Morton, R. K., editors.

Felton, Ronald H. and Linschitz, Henry   2, 16
                                                    CA 64-13762h (1966)

Polarographic reduction of porphyrins and electron spin resonance of
porphyrin anions. (Harvard Univ.).   J. Am. Chem. Soc. 88 (6), 1113-16
(1966) (Eng).   Polarographic measurements were made on a no. of tetra-
phenylporphyrin and etioporphyrin complexes, in $HCONMe_2$ or Me_2SO soln.
The polarograms are characterized by 2 main waves corresponding, for
the most part, to 1-electron redns.   This is confirmed by the optical
and E.S.R. absorption of porphyrin monoanions, prepd. by electrochem.
redn. at the 1st half-wave potential.   Evidence is given that addn. of
both electrons generally occurs into orbitals belonging mainly to the
porphyrin ring, except for Co tetraphenylporphyrin, in which redn.
appears to occur in a metal-centered orbital.   These results, and the
observed order of increasing neg. half-wave potentials (corresponding
to the calcd. order of overall neg. charge on the ring), are in agree-
ment with recent theoretical results of Zerner and Gouterman (CA 64,
7385f).   The monoanion E.S.R. spectra fall into 2 classes, differing
sharply in line breadth and g value.   The line widths are discussed.

Ferguson, Lloyd N.   1, 13
                                                    CA 43-2923e (1949)

Relationships between absorption spectra and chemical constitution of
organic molecules.   Chem. Revs. 43, 385-446 (1948).   A review with 312
references.

Ferguson, Lloyd N.   CA 47-3327b (1953)

Electron Structures of Organic Molecules.   New York: Prentice-Hall.
1952.   335 pp.

Fernandez, Jose and Becker, Ralph S.   1, 17, 15
                                                CA 54-2934f (1960)

Unique luminescences of dry chlorophylls.   (Univ. of Houston, Texas).
J. Chem. Phys. 31, 467-72 (1959); cf. C.A. 49, 12969h.   Dry chloro-
phylls a and b in a rigid glass hydrocarbon solvent have intense emis-
sion at 7550 and 7330 A, resp.   In each case the room-temp. absorption
spectra show the presence of a band shoulder on the long wavelength
side of the main red band.   Both the emission and the absorption bands
disappear in the presence of hydroxylic solvents.   The absorption and
emission are interpreted as $n-\pi^*$ singlet and $n-\pi^*$ triplet transitions,
resp.   The lifetime of the $n-\pi^*$ triplet emission in chlorophyll a is
estd. to be 10^{-3} sec. Cu chlorophyll b has an intense phosphorescence
at 8740 A with a lifetime of less than 10^{-4} sec.   The differences in
the room-temp. emission spectra for chlorophylls a and b are discussed.

Fielding, P. E. and MacKay, A. G.   1, 4
                                                CA 59-10892e (1963)

Electrical and optical properties of the phthalocyanines.   (Univ. New
England, Armidale, Australia).   J. Chem. Phys. 38 (11), 2777-8 (1963).
Measurements were carried out on thin single crystals prepd. from puri-
fied phthalodinitrile soln.   Relatively strong absorption bands were
observed, 8000-10,000 cm^{-1}, in metal-free, Cu, and Ni phthalocyanines
and weak absorption for Co phthalocyanine.   Stronger bands were ob-
served, 5000-7000 cm^{-1}, in Co and Ni phthalocyanines.   A band at 6410
cm^{-1} in the spectrum of the Ni compd. was attributed to a d-d type of
transition.   No phosphorescent emission was detected, 5000-7000 cm^{-1},
when the compds. were cooled to -175°.   Some of the results of Day and
Williams (CA 58, 1056f) could not be reproduced.   The difference in
results was attributed to the introduction of surface states when the
compd. was powdered.

Fink, Hermann and Hoerburger, Wolfgang   2, 15
                                                CA 27-5643 (1933)

The fluorescence of the porphyrins.   II.   Z. physiol. Chem. 220, 123-
36 (1933); cf. C.A. 27, 4255.   Detn. of p_H fluorescence curves affords
a means of distinguishing the various porphyrins on the basis of the
no. of carboxyls present.   Etioporphyrin and its mono-, di-, tetra-
and octacarboxylic acids give characteristic curves which are easily

distinguished. The min. fluorescence is at the isoelec. point, which shifts to the acid side with increasing no. of carboxyls. The variations are most conspicuous in the alk. branch of the curve, except with etioporphyrin, which has no alk. branch because of the absence of carboxyl. The curves represent roughly the dissocn. of ampholytes, the deviations at the isoelec. point being due to the presence of pigment dispersed in colloidal rather than mol. form.

Fink, Hermann and Hoerburger, Wolfgang   2, 15
                                                CA 27-4255 (1933)

The fluorescence of porphyrins. I. Z. physiol. Chem. 218, 181-201 (1933). p_H-Fluorescence curves are plotted for the 4 isomeric coproporphyrins and the 3 uroporphyrins, and the influence of such factors as concn., inorg. salts, temp. and soly. is discussed.

Egg lecithin and plant lecithin. The question of their similarity in a physiological respect. Kurt Dragendorff. Chem.-Ztg. 57, 493-4 (1933).

Fink, H. and Hoerburger, W.   2, 15

Beitrage Zur Fluorescenz Der Porphyrine IV. Z. Physiol. Chemistry, 232 (1935) p. 28.

Fleischman, Darrell E. and Tollin, Gordon   1, 8
                                                 CA 62-8046b (1965)

Molecular complexes of flavines and phenols. I. Absorption spectra and properties in solution. (Univ. of Arizona, Tucson). Biochim. Biophys. Acta 94 (1), 248-57 (1965)(Eng). We have found that alloxazine derivs., such as lumichrome, FMN and riboflavine, yield highly colored solns. in strong acid with electron-rich phenols due to the formation of 1:1 charge-transfer complexes between the phenol and the monoprotonated flavine. With very good donors, 1, 4-naphthalenediol or trimethylhydroquinone, similar complexes also form in neutral soln. The position of the charge-transfer absorption band, in soln. and in crystals of the complexes, varies with the donor properties of the phenol. E.P.R. studies indicate the presence in acidic soln. of low concns. of the flavine semiquinone.

Fleischman, Darrell E.   1, 8
and Tollin, Gordon   CA 63-3027g (1965)

Molecular complexes of flavine and phenols. III. Factors influencing
spectra and stability. (Univ. of Arizona, Tucson). Proc. Natl. Acad.
Sci. U.S. 53 (1), 38-46 (1965)(Eng); cf. CA 62, 8046b. Stability
consts. of flavin complexes were detd. Correlations between stabili-
ties, charge transfer band positions, and the structures and electronic
properties of the components helped elucidate the nature of the bonding
in the complexes. Estns. from the mol. orbital theory found the posi-
tion of the charge transfer band of flavin-naphthalenediol complexes in
acidic soln. to be a monotonic function of the ionization potential of
the donor. Flavin-phenol complexes in neutral soln. had a 1:1 flavin-
phenol ratio, whereas cryst. complexes had a 1:2 ratio. Stability
consts. ranged from 1 to 250, neutral complexes being more stable than
acid. Charge transfer did not contribute significantly to the stabili-
zation of the acid complexes.

Foersterling, H. D. and Kuhn, H.   1, 4, 10
                                                CA 63-7769b (1965)

Calculation of absorption spectra of a phthalocyanine in various pro-
ton stages and of a tetrabenzoporphine. (Univ. Marburg, Ger.).
Chimia (Aarau) 19 (5), 322-4 (1965)(Ger). In solns. of Cu 4,4',4'',4'''-
phthalocyanine-tetrasulfonate (P) in acids (H_2O-H_2SO_4, H_2SO_4-oleum,
HOAc-H_2SO_4, dioxane-H_2SO_4), the forms $P(H^+)_1$, $P(H^+)_2$, $P(H^+)_3$, and
$P(H^+)_4$, can be differentiated spectroscopically. The spectra of these
forms and the monomeric nonproton form (P) and Zn tetrabenzoporphine
are compared and calcd.

Forti, Giorgio, Bertole, Maria Luisa   1, 5, 12
and Parisi, Bruno   CA 59-1962h (1963)

Function of cytochrome f in photosynthetic electron transport. (Univ.
Milan). Biochem. Biophys. Res. Commun. 10, 384-9 (1963). The redn.
of cytochrome f by chloroplasts in the presence of light was demon-
strated. A phosphorylating site is situated during the transfer of
electrons from H_2O to cytochrome f through the light reaction. One
mol. of adenosine triphosphate is formed for each electron pair trans-
ferred.

Frackowiak, D. and Trumpaka, Z.   1, 15, 17
                                                   CA 61-13564c (1964)

Polarization of fluorescence of chlorophyll a.   (N. Copernicus Univ.,
Torun). Bull. Acad. Polon. Sci., Ser. Sci., Math., Astron. Phys. 12
(3), 183-7 (1964). The degree of polarization of fluorescence of
chlorophyll a solns. in 4 solvents (Plexiglas dissolved in benzene,
collodion, Et_2O, and isoamylamine) was measured, in the wavelength
region 3900-4500 A (Soret band). Absorption spectra are given and also
a plot of the emission anisotropy. The plot revealed 4 transitions of
alternating polarization within the single broad band exhibited in the
absorption spectrum. The exptl. results were in qual. agreement with
calcns. using the linear combination of atomic orbitals-mol. orbital
method, with configuration interactions taking into account 4 mol.
orbitals. Overlapping of more than 2 electronic transitions in the
region of the Soret band apparently occurs.

Frackowiak, D. and Kaminska, M.   1, 17
                                                   CA 59-865g (1963)

Influence of chlorophyll a aggregation in its short-wave band.   (N.
Copernicus Univ., Torun, Poland). Bull. Acad. Polon. Sci., Ser. Sci.,
Math., Astron. Phys. 10, 601-3 (1962)(in English). Absorption curves
of 8 chlorophyll a solns. in collodion showed that absorption in the
short-wave band decreases as the concn. of pigment increases. For dil.
solns. ($10^{-6}M$) the absorption amts. to about 120 l./g. cm., whereas
for concd. ones ($5 \times 10^{-4}M$) it does not exceed 37 l./g. cm. The
absorption band widens as the concn. of the soln. increases, with the
max. at about 4100 A increasing more than the max. at about 4300 A.
The results indicate that the aggregation of chlorophyll leads to the
splitting of the short-wave absorption band, as well as to the changes
in the shape of the long-wave band (Brody and Brody, CA 55, 13551h).
The changes are probably due to the dimers of the pigment with absorp-
tion maxima situated on both sides of the band given by the monomers.
The results, obtained for solns. of viscosity of about 3 poises, were
not observed in solns. with viscosity of about 30 poises.

Frackowiak, D.   1, 17
                                                   CA 62-1892f (1964)

Absorption spectra of chlorophyll a at low temperature.   (N. Copernicus
Univ., Torun). Bull. Acad. Polon. Sci., Ser. Sci., Math., Astron.
Phys. 12 (6), 357-9 (1964)(Eng). Absorption spectra at room temp.
(20°) and at low temps. (-70 and -190°) were given for chlorophyll a
in collodion and castor oil. The solns. did not emit slow fluorescence.
The decrease in temp. caused narrowing of the band and a shift toward
longer wavelengths. This was attributed to the formation of aggregates
of chlorophyll.

Frackowiak, D.   15, 17
                                                   CA 61-13564f (1964)

<u>Luminescence of chlorophyll.</u> Postepy Fiz. 14 (5), 549-67 (1963); cf.
CA 60, 10078h. A review with 41 references.

Frackowiak, D. and Marszalek, T.   15, 17
                                                   CA 59-131e (1963)

<u>Yield of anti-Stokes fluorescence of chlorophyll.</u> (N. Copernicus
Univ., Torun, Poland). Bull. Acad. Polon. Sci., Ser. Sci., Math.,
Astron. Phys. 9, 53-5 (in English). The fluorescence yields of chloro-
phyll a in ether were measured in the range 6000-7040 A.

Frackowiak, D. and Marszalek, T.   15, 17
                                                   CA 57-4195c (1962)

<u>Yield of the fluorescence and spectra of chlorophyll in viscous media.</u>
(Univ. Torun, Poland). Bull. Acad. Polon. Sci., Ser. Sci.,Math.,
Astron. Phys. 8, 713-7 (1960) (in English). Intensity distribution of
fluorescence exited with a high-pressure Hg lamp was examd., 6100-
7300 A, for chlorophyll a in collodion of 3.8 and 31 poises viscosity
and in ether soln. Both solns. gave practically the same absorption
and emission spectra, displaced by about 50 A as compared with those
in ether soln., as well as very similar curves of fluorescence yield
vs. wavelength.

Freed, Simon and Hochanadel, C. J.   1, 3
                                                      CA 44-433h (1950)

Absorption spectrum of β-carotene in liquid solution at the temperature
of liquid nitrogen. Science 110, 298 (1949); cf. C.A. 43, 8881a. A
solvent composed of equal vols. of liquid propane and propene dissolved
carotene rapidly at -50° and maintained it at -196° in sufficient concn.
for investigation. A hydrocarbon solvent does not possess a permanent
elec. dipole moment which would distort solute mols. The spectrum at
-196° differed considerably from hexane soln. at room temp. The no. of
absorptive peaks were the same, but their relative intensities differed
greatly. They were much sharpened and in general displaced toward long
wavelengths at the low temp. The solute contained 10% α-carotene.

Freed, Simon and Sancier, Kenneth M.   1, 17
                                                      CA 46-3855i (1952)

Absorption spectra of chlorophylls in solutions at low temperatures.
Equilibrium between isomers. (Brookhaven Natl. Lab., Upton, N.Y.).
Science 114, 275-6 (1951). The absorption spectra of chlorophyll a,
chlorophyll b, and chlorophyll b' were measured over a range of temps.
from 300° to 75°K. At room temp. the spectra agreed with those
previously reported except that in the spectrum of chlorophyll b' 4
weak bands in the ultraviolet region are superimposed on a greater gen-
eral absorption than is exhibited in this region by chlorophyll b.
The solvent for all the chlorophylls at low temps. consisted of 20% by
vol. of dipropyl ether, 40% propane, and 40% propene. The solvent
employed above 230°K was 20% dipropyl ether and 80% hexane. There
must be at least one other component in chlorophyll b. The difference
in the spectra of the chlorophylls in different solvents (especially
in the region of 4100-4300 A.) may be largely due to the change in
relative concns. of isomers present in equil.

Freed, Simon   1, 11, 17
                                                      CA 53-17217h (1959)

Chemistry and biochemistry at low temperatures and discrimination of
states and reactivities. (Brookhaven Natl. Lab., Upton, N.Y.).
Symposium Inform. Theory Biol., Gatlinburg, Tenn. 1956, 171-9 (Pub.
1958). Properties of some substances, chemical and biological, at
low temps. are discussed. Abs. spectra of $PrCl_3$ at room temp. and that
of liquid N and He; of carotene at room temp. and at 77°K, in suitable
solvents; and of chlorophyll b at room temp. and at 300°K, 230°K, 180°K,
and 75°K in various solvents are discussed. These and many other
observations are quoted to show that reactions do take place at low
temps. Investigations at low temps. may yield much knowledge in biol.
fields also, if the problem of finding solvents is solved.

Frei, Yael F.   1, 17
CA 57-1275g (1962)

Derivative absorption spectra of chlorophyll in algae and leaves at
low temperatures. (Carnegie Inst. of Washington, Stanford, Calif.).
Biochim. Biophys. Acta 57, 82-7 (1962)(in English). Chlorophyll a in
live plants was found in several spectrophotometrically distinct com-
binations, difficult to recognize because of strongly overlapping
absorption bands. The bands could be distinguished through deriv.
spectrophotometry, esp. at low temps. where the bands were sharpened
and smaller amts. of minor components could be detected than at room
temp. Deriv. absorption spectra were detd. for several algae and
leaves at room temp. and -180°. At low temp. a shoulder with a max.
near 655 mµ, representing an unidentified component, was observed in
the spectra of Porphyridium cruentum, Phormidium persicinum, and
lettuce leaf.

French, C. S.; Smith, J. H. C.;   15, 13, 17
Virgin, H. I. and Airth, R. L.

Fluorescence-Spectrum Curves of Chlorophylls, Pheophytins, Phycoerythrins,
Phycocyanins and Hypericin. Plant Physiology, 31 (1956) p. 369.

Friedel, Robert A. and Orchin, Milton

Ultraviolet Spectra of Aromatic Compounds, New York, Wiley, c 1951

French, C. S.   12
CA 55-13485g (1961)
Light, pigments, and photosynthesis. (Carnegie Inst. of Washington,
Stanford, Calif.). Ibid. 447-71. IN: Symposium on Light and Life,
Johns Hopkins University, 1960 Light and Life; proceedings. Edited
by William D. McElroy and Bentley Glass. (Johns Hopkins University.
McCollum-Pratt Institute. Contribution No. 302).

Fuller, R. C.; Conti, S. F.   12
and Mellin, D. B.   Bacterial Photosynthesis-
Part I

The Structure of the Photosynthetic Apparatus in Green and Purple Sulfur
Bacteria. Bacterial Photosynthesis - Howard Gest, Anthony San Pietro,
and Leo P. Vernon (ed.)

7129-Final   127

Gachkovskii, V. F.
15, 17
CA 57-14156c (1962)

The fluorescence spectra of the photoreduced forms of chlorophyll and pheophytin. (Acad. Sci. U.S.S.R., Moscow). Biofizika 4, 16-23 (1959). The fluorescence spectra of the photoreduced forms of chlorophylls (a + b) and a, and of pheophytins (a + b) and a were studied. The fluorescence spectra of pheophytins (a + b) and a were found to be the same (at concns. of 2 X 10^{-5}M); so were those of photoreduced chlorophylls (a + b) and a, and of photoreduced pheophytins (a + b) and a. Energy could be transferred in true solns. from pheophytin b, from photoreduced chlorophyll b, and from photoreduced pheophytin b, to pheophytin a, to photoreduced chlorophyll a, and to photoreduced pheophytin a, resp. The structures of the photoreduced forms were established from the fluorescence spectra, the primary photoreduced forms of pheophytins (a + b) and a gave peaks at 662 and 733 mμ, which peaks lie nearly at the same points as do the peaks in the long-wave region in the secondary forms (643, 644, and 733 mμ). The secondary forms of chlorophylls (a + b) and a had peaks at 620, 651, and 731 mμ. The peaks at about 730 mμ given by photoreduced pheophytins and chlorophylls intensifed rapidly when the solns. were cooled. These peaks behaved quite differently from all the others, which did not change appreciably with temp. From Biol. Abstr. 36, Abstr. No. 5595 (1961).

Gachkovskii, V. F.
1, 15, 4, 17
CA 48-6828 (1954)

Absorption spectra and fluorescence spectra of chlorophyll and magnesium phthalocyanine in the adsorbed state. (A. N. Bakh Biochem. Inst., Acad. Sci. U.S.S.R., Moscow). Doklady Akad. Nauk S.S.S.R. 93, 511-14 (1953); cf. C.A. 45, 3248b; 46, 6940d. Absorption spectra obtained by diffuse scattering from specimens of Mg phthalocyanine adsorbed on MgO in EtOH or Et_2O were observed after heating the adsorbate to 375° to remove the red fluorescence; the adsorbate initially has a blue color, which disappears on such heating. The specimens were subjected to action of O or various org. solvents, and the resulting spectra are shown. The results clearly show the same origin of both absorption and fluorescence spectra. When the vapors of Mg-free phthalocyanine are adsorbed on MgO, and the adsorbates are exposed to O, fluorescence does not occur. Similar expts. could not be run with chlorophyll owing to its low order of stability on MgO. However, repeated evacuation at 20° of adsorbates of chlorophyll on MgO from Et_2O gave specimens which displayed a widening of the main absorption max. in the direction of shorter wavelengths, while passage of O into such prepns. increased the intensity of absorption in 625-50 mμ region for fluorescence and 620-40 for absorption spectra. Adsorption of EtOH, Et_2O, or H_2O onto such specimens, followed by evacuation, led to disappearance of the main fluorescence band and

appearance of a sharp max. at 648 mμ, which corresponds to a max. of
666 mμ of the fluorescence spectrum of the product of the dark process;
in case of H_2O this max. gradually shifts to 671 mμ. With Mg phthalocya-
nine the shift is to 684 mμ. Generally under conditions which preclude
total destruction of the mols., the events observed with adsorbates of
chlorophyll are paralleled by those of Mg phthalocyanine.

Gaffron, Hans   12
                                                              CA 52-10302g (1958)

Research in photosynthesis. (Univ. of Illinois, Urbana), A. H. Brown,
C. S. French, R. Livingston, E. I. Rabinowitch, B. L. Strehler, and
N. E. Tolbert, editors. Natl. Acad. Sci.-Natl. Research Council, 1955,
524 pp. (Pub. 1957).

Gaines, G. L., Bellamy, W. D.,   1, 17
and Tweet, A. G.   CA 61-6541g (1964)

Interaction between chlorophyll a and fatty alcohol molecules in mixed
monomolecular films. (Gen. Elec. Res. Lab., Schenectady, N. Y.). J.
Chem. Phys. 41 (2), 538-42 (1964). Chlorophyll a and oleyl alc. form
nearly ideal 2-dimensional solns., up to a chlorophyll mole fraction of
at least 0.2. Chlorophyll is essentially insol., however, in stearyl
alc. monolayers at room temp. Measurements of collapse pressure, area,
absorption spectrum, and fluorescence spectrum of the monolayers con-
firm these conclusions. The fluorescence and absorption spectra of
concd. and dild. (in oleyl alc.) chlorophyll films are compared.
Measurable shifts in both absorption and emission demonstrate that
chromophore-chromophore interactions are detectable in monolayers
contg. high chlorophyll concns.

Gest, Howard and Bose, Subir K.   11, 12

Structure and Function in Bacterial Photosynthesis. Bacterial
Photosynthesis - Howard Gest, Anthony San Pietro, and Leo P. Vernon (ed.)

Gibson, J. F. and Ingram, D. J. E.   2, 11, 13, 16
                                                              CA 51-10232a (1957)

Location of free electrons in porphine ring complexes. (Univ. Southampton,
Engl.). Nature 178, 871-2 (1956). Electron resonance measurements dur-
ing oxidation of hemoglobin, myoglobin, tetraphenylporphine, phthalocya-
nine, and diphenylpicryl-hydrazyl showed similar absorption spectra with
g-values about 2.0023. Therefore, the oxidation state is one contg. an

unpaired electron mobile in the conjugated ring structure. No hyperfine structure occurred in the spectra from the porphine intermediate, showing that the orbit of the unpaired electron is not confined near the nitrogens in the center of the ring but includes most of the C atoms.

Gilliam, A. E. and Stern, E. S.

1
CA 52-8754f (1958)

An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry. 2nd ed. London: Edward Arnold. 1957. 326 pp. 50s.

Giraud, Georges

15, 11
CA 61-6047c (1964)

Fluorescence in vivo of some marine algae. (Ecole Norm. Super., Paris). Proc. Intern. Seaweed Symp., 4th, Biarritz, France 1961, 326-30 (Pub. 1964)(in French). As in green algae and in the chloroplasts of higher plants, a peak of fluorescence was found at about 720 mμ in Rhodosorus marinus and Stichochrysis. It increased greatly at low temps., esp. at -190°. This may be explained by the presence of 2 forms of chlorophyll a. The effect of low temp. may result from a decrease in thermal inactivation.

Godnev, T., Akulovich, N. K.
and Rotfarb, R. M.

11, 17
CA 59-5414e (1963)

Complete synthesis of chlorophyll and its biosynthesis. Usp. Sovrem. Biol. 55(2), 204-18 (1963). A review with 32 references.

Goedheer, J. C.

1, 15, 11, 17
CA 63-3316c (1965)

Fluorescence action spectra of algae and bean leaves at room and at liquid-nitrogen temperatures. (State Univ., Utrecht, Neth.). Biochim. Biophys. Acta 102 (1), 73-89(1965)(Eng). Fluorescence action spectra were detd. at room temp. and at liquid-N temp. with various blue-green, red, and green algae and greening bean leaves. Fluorescence at room temp., with a max. at about 685 mμ, was for the greater part emitted by a short wave "form" of chlorophyll a, possibly C_a670. To this form energy was transferred from β-carotene, chlorophyll b, and phycobilins with an efficiency approaching 100%. The action spectra of blue-green algae suggested the presence of a 650-mμ phycocyanin "form" which seemed bound more firmly to the photosynthetic app. than the bulk of phycocyanin absorbing around 620 mμ. The absence of action in the

carotenoid region in blue-green and red algae and in bean leaves shortly after transformation of protochlorophyll to chlorophyll was ascribed to the presence of a high percentage of xanthophyll, presumably inactive in transferring energy to chlorophyll. All pigments active in producing the 685-mμ room-temp. fluorescence band were found to be active in producing the 720-mμ low-temp. fluorescence band. Addnl. the 720-mμ fluorescence band was excited by absorption in long wavelength chlorophyll a forms (e.g. $C_a 680$ and $C_a 695$) and, in blue-green and red algae, by one or more unidentified pigments with absorption max. at 475 and 520 mμ. Marked differences between high-d. action spectra of blue-green and green algae are described.

Goedheer, J. C.   1, 17, 15
                                                               CA 61-14946h (1964)

<u>Fluorescence bands and chlorophyll a forms.</u> (State Univ., Utrecht, Neth.). Biochim. Biophys. Acta 88 (2), 304-17 (1964)(in English). Fluorescence spectra were detd. at temps. between 20° and -196° for a no. of photosynthetic organisms. Below -90° the single fluorescence max. around 685 mμ was replaced by a system of 3 bands, at 686, 696, and 717-20 mμ in algal cells. Cooling usually resulted in a decrease of the 685-mμ band. In young cultures of blue-green and red algae the 3 bands were of about equal intensity; in old cultures and in green algae the 717-mμ band was dominant, while in the latter the 696-mμ band was weak. In green leaves and chloroplasts also, 3 bands were present at low temps., at 686, 696, and 735-40 mμ. Here too, the 740-mμ band was by far the major one. During cooling of both dild. and concd. chlorophyll a solns. and chlorophyll adsorbed on filter paper, the height of the 677-mμ fluorescence band and the 730-mμ vibrational level were increased by a factor of about 2, provided no increased reabsorption due to increased scattering could occur. In concd. chlorophyll a solns. no extra bands could be detected. The 3 fluorescence bands measured in vivo at low temps. are assumed to belong to 3 chlorophyll a forms: C_a 670-F 686; C_a 680-F 696; C_a 695-F 717 in algal cells. Apart from an increase in intrinsic fluorescence yield of C_a 695, the marked increase in 717-mμ fluorescence during cooling is suggested to be due to increased energy transfer from C_a 670 and C_a 680 to C_a 695 as a result of shrinkage, when the temp. is lowered.

Goedheer, J. C.   1, 17, 11
                                                    CA 50-6931g (1956)

Chlorophyll spectra and molecular structure. (Biophys. Research Group,
Utrecht, Neth.). Nature 176, 928-9 (1955). The absorption spectrum
and fluorescence polarization spectrum of bacteriochlorophyll and
bacteriopheophytin in cyclohexanol were obtained from 400 to 800 mμ.
The absorption and polarization spectrum of chlorphyll a and pheophytin
a is also given for the same region. The observed spectra are compared
with calcd. spectra for bacteriopheophytin and tetrahydroporphin.

Goodwin, T. W.   11, 3
                                                    CA 55-4597a (1961)

Algal carotenoids. (Univ. Coll. Wales, Aberystwyth). Symposia Comp.
Biol. Kaiser Foundation Research Inst. (Mary B. Allen, editor.
Academic Press) 1, 1-10 (1960). Comparative Biochemistry of Photo-
reactive Systems (V.1 of Symposia on Comparative Biology) Mary Belle
Allen, ed., New York Academic Press, 1960.

Gouterman, Martin and Stryer, Lubert   2, 15, 10
                                                    CA 58-3012g

Fluorescence polarization of some porphyrins. (Harvard Univ.). J.
Chem. Phys. 37, 2260-6 (1962). Fluorescence-polarization data on
porphyrins can be interpreted in terms of the theory of polarization
spectroscopy and the theory of the electronic and vibrational structure
of these mols. These 2 theories combine to interpret most of the data
but some anomalies remain. The results hint at the richness of data
that can be expected from fluorescence-polarization expts. when tech-
niques are developed further.

Gouterman, Martin; Wagniere, Georges   10, 2
and Snyder, Lawrence C.   CA 59-13451d (1963)

Spectra of porphyrins. II. Four-orbital model. (Harvard Univ.). J.
Mol. Spectry. 11 (2), 108-27 (1963); cf. CA 55, 20615d. A quant.
attempt is made to apply a 4-orbital model, described earlier (loc.
cit.), to prophyrin mols. The model is a combination of L.C.A.O.-M.O.
and a simplified treatment of configuration interaction. The parame-
ters for the latter are detd. on Zn tetraphenylporphine. Orbital and
transition energies and oscillator strengths are detd. for the reduced
porphyrins: dihydroporphine, tetrahydroporphine, hexahydroporphine,
and octahydroporphine. Qual. agreement with the observed spectra is
obtained. Similar calcns. are made for phlorin-6-dihydrochloride.

Spectra calcns. are given for the metal salts of mono-, di-, and triazaporphine, tetrabenzoporphine, tetrabenzotetraazaporphine (or phthalocyanine), and monobenzo-, 2 dibenzo-, and tribenzotetraazaporphine. The calcns. are in fair agreement with observed spectra. Quant. applications of the model are limited to regions of small perturbations. The application of the model to the calcn. of chem. and magnetic properties is discussed.

Gouterman, Martin   1, 2, 10
                                                     CA 53-16690b (1959)

Effects of substitution on the absorption spectra of porphin. (Univ. of Chicago). J. Chem. Phys. 30, 1139-61 (1959). A model was presented for the excited states of porphin, which are viewed as arising from 2 configurations which can be mixed to varying degrees. The effects of substituents are discussed, 1st the limitations imposed by symmetry requirements and then the requirements imposed if they act as 1-electron perturbations. The theory is applied to exptl. problems. The metal porphins can be viewed as a series showing increasing mixing of the 2 fundamental configurations. The effect of free base formation is explained as a cyclic polyene perturbation. This theory predicts that the lowest porphin transition is polarized parallel to the H-H axis. Formulas are derived for intensity changes caused by various external substituents. Formulas are developed to account for the effects of aza substitution on the methine bridges.

Gouterman, Martin   1, 2, 10
                                                     CA 55-20615d (1961)

Spectra of porphyrins. (Harvard Univ.). J. Mol. Spectroscopy 6, 138-63 (1961). Absorption spectra for 3 series of porphyrins derived from the basic skeleton are given: (a) compds. obtained by simple substitution; (b) compds. obtained by redn. of 1 or more pyrrole rings; and (c) compds. obtained from fusion of aromatic rings onto the basic skeleton. The spectra are discussed in terms of a 4-orbital model. Intensity changes and energy shifts are related to the properties of 2 top filled and 2 lowest empty π orbitals. Emission spectra of metal porphyrins are discussed. In closed shell metals, the continuous enhancement of phosphorescence at the expense of fluorescence is attributed to spin-orbit coupling. In paramagnetic metals, observed effects are attributed to the existence of a state at the same energy as the usual triplet, but with multiplicity the same as the ground state; its intensity is ascribed to exchange interactions. In diamagnetic metals with unfilled d shells, peculiar emission properties are attributed to enhanced spin orbit coupling due to low-lying metal triplets.

Govindjee and Govindjee, R.   1

Action Spectra for the Appearance of Difference Absorption Bands at
480 and 520 mμ In Illuminated Chlorella Cells and Their Possible
Significance to a Two-Step Mechanism of Photosynthesis.

Granick, S.   17, 11

Magnesium Protoporphyrin as a Precursor of Chlorophyll in Chlorella.
Journal of Biological Chemistry, 175 (1948) p. 333-342.

Granick, S., Bogorad, Lawrence,   9, 17, 11
and Jaffe, Herbert

Hematoporphyrin IX, A Probable Precursor of Protoporphyrin in the
Biosynthetic Chain of Heme and Chlorophyll. Journal of Biological
Chemistry, 202 (1953) p. 801-813.

Granick, S.   11, 17

Magnesium Vinyl Pheoporphyrin a5, Another Intermediate in the Biological
Synthesis of Chlorophyll. Journal of Biological Chemistry, 183 (1950)
p. 713-30.

Granick, S.   9, 11, 17
                                                    CA 63-16630d (1965)

Evolution of heme and chlorophyll. (Rockefeller Inst., New York,
N.Y.). Evolving Genes Proteins, Symp. Rutgers, State Univ. 1964,
67-88 (Pub. 1965)(Eng). A review with 33 references.

Granick, S. and Mauzerall, D.   9, 17, 11
                                                     CA 56-3750a (1962)

Metabolism of heme and chlorophyll. (Rockefeller Inst., New York).
Ibid. 525-616.

Granick, S.   11, 17, 12
                                                     CA 59-8997a (1963)

The pigments of the biosynthetic chain of chlorophyll and their inter-
actions with light. (Rockefeller Inst., New York, N. Y.). Proc. Intern.
Congr. Biochem., 5th, Moscow, 1961, 6, 176-86 (Pub. 1963)(in English).
A review with 40 references.

Gribova, Z. P., Umrikhin, V. A., and 	1, 2
Kayushin, L. P. 	CA 64-17919a (1966)

Participation of triplet excited state in photoreactions of porphyrin
at 77°K. (Inst. Biol. Phys., Moscow). Biofizika 11 (2), 353-5 (1966)
(Russ). The effect of interrupted illumination on the production of
free radicals in an EtOH soln. of Mg etioporphyrin (I) in 10^{-4}-10^{-3}M
concn. was studied. Illumination was carried out with a full-spectrum
Hg lamp. Results established participation of a chromophore triplet
excited state in free radical formation. Similar results were obtained
with an EtOH soln. of Zn tetraphenylporphyrin.

Grigoryan , A. N., Nekrasov, L. I. 	17, 13
and Kobozev, N. I. 	CA 66-5966z (1966)

Reversible color change of chlorophyll and pheophytin during their
adsorption on magnesium oxide. (State Univ., Moscow). Vestn. Mosk.
Univ., Ser. II, Khim. 21 (3), 42-4 (1966)(Russ). During adsorption
of chlorophyll and pheophytin from Et_2O on activated (by the thermal
treatment at 450°) MgO the reversible change of color of the adsorbates
was observed and measured spectrophotometrically. The mols. of the
above pigments probably form complex compds. with Et_2O mols. on the
MgO surface.

Gurinovich, G. P. and Sinyakov, G. N. 	2, 13, 15
  	CA 64-6439g (1966)

Polarized luminescence of the photochemical reaction products of
porphyrins. (Phys. Inst., Minsk). Biofizika 10 (6), 946-52 (1965)(Russ);
cf. CA 60, 8269b. Mesoporphyrin (I) was photoreduced by ascorbic acid
(II) in pyridine-EtOH (1:7) and in 60 or 80% H_2SO_4. The reversibly
reduced product (III) had new absorption bands at 740, at 510, and at
450 and 510 mμ for the three solvents, resp., with low temp. luminescence
bands at 810, at 530, and at 470 and 530 mμ. The max. polarization of
luminescence, P_0, of III was 38-47% in all solvents, showing that there
is no symmetry greater than 2-fold. Tetraphenylporphyrin (IV) was
photoreduced by II to give a reduced product (V) having new absorption
bands at 700 and 450 mμ for redn. in pyridine-EtOH (1:1) and at 700
and 775 mμ in a (1:7) mixt. The low temp. luminescence max. of V was
at 765 and at 840 in these solvents, resp. From high values of P_0, V
is of no greater than 2-fold symmetry. Protoporphyrin (VI) was photo-
oxidized in air to give a reversibly oxidized form (VII) with an
absorption max. at 670 and luminescence at 679 mμ. From the shape of
the P_0 spectra, III formed in pyridine-EtOH and V has only 1 electronic
transition each above 470 mμ, but I and IV have 2 each with perpendicular

transition moments. In III and V the Soret transition moments are perpendicular to the red band moments. The sign of P_O for III formed in acid does not change from the highest exciting λ down to 360 mμ. The P_O spectrum of VII suggests that the photooxidation of VI gives a chlorin-type intermediate.

Gurinovich, G. P., et al   1, 17
                                                            CA 52-1762c (1958)

Optical properties of chlorophyll and metal derivatives of pheophytine.
Optika i Spektroskopiya 3, 237-45 (1957). The comparison of absorption
and polarization spectra of chlorophyll (I) (obtained chromatographi-
cally from Urtica), chlorophylide (II) (by fermentation from Heracleum
leaves), pheophytine (III) (prepd. by the method of Godnev).

Gurinovich, G. and Patsko, I.   2, 1, 15
                                                            CA 59-14751a (1963)

Application of pulse-spectroscopy methods to the study of porphyrins.
Izv. Akad. Nauk SSSR, Ser. Fiz 27 (6), 772-6 (1963). Mesoporphyrin,
its Zn and Cu derivs., protoporphyrin, and tetraphenylporphine and
its Zn and Cu derivs., dissolved in pyridine, toluene, iso-BuOH, iso-
PrOH, and Me methacrylate were subjected to light pulses of 3 x 10^{-4}-sec.
duration and variable pulse repetition rate. The max. of irradiated
samples are shifted; in tetraphenylporphine in Plexiglas, e.g., the
Soret band is shifted from 435 to 460 mμ and bands at 520, 550, 592,
and 647 mμ to 680 and 770 mμ. The spectrum of pulse-irradiated Zn
tetraphenylporphine is completely changed from bands at 437 (intense),
569, and 594 mμ to bands at 487 (intense), 582, 612, and 785 (intense)
mμ. The other substances have similar spectra. Measurements were
made of the times necessary for bleaching and for the formation of
addnl. absorption. These are tabulated for all materials. There is
a delay of ~300 μsec. between bleaching and the formation of new
absorption max. This delay probably corresponds to the photochem.
reaction of electron transfer from the solvent to the porphyrin mol.

Gurinovich, G., Pateeva, M. V.,   2, 15
and Shul'ga, A. M.   CA 59-14761d (1963)

Spectral luminescent investigation of photochemical porphyrin trans-
formations. Izv. Akad. Nauk SSSR, Ser. Fiz. 27 (6), 777-81 (1963).
Photochem. transformations of porphyrins were studied on their solns.
in pyridine, alc., their mixts., and mixts. with H_2O, and also in
acetone and H_2O, using ascorbic acid as reducer (approx. 50 mg. per

10cc.). In the absorption spectra of mesoporphyrin, the bands at 500, 530, 570, and 620 mμ are weakened after 4 irradiations with a 500-w. lamp and new broad bands appear at 660 and 740 mμ, as well as between the Sauret band and 550 mμ band. Increase of H_2O in the pyridine + H_2O solvent decreases the time for equal change in spectral intensity. No changes are observed with pyridine alone. Admission of air to the evacuated soln. restores the original situation. Alc. is still stronger acting in mixts. with pyridine. Luminescence spectra are also changed by redn. owing to illumination. Similar effects were observed on protoporphyrin. Photoreduction is very rapid in porphine and similar in nature to the preceding observations. No photochem. changes were observed on benzoporphine and tetraazatetrabenzoporphine. Tetraphenyl-porphine must be irradiated for 15-30 min.

Gurinovich,G. P., Patsko, A. I.,　　　　　　2, 15
Solov'ev, K. N. and Shkirman, S. F.　　　　CA 63-17339b (1965)

Polarization of the phosphorescence of metal-porphyrins. Optika i Spektroskopiya 19 (2), 239-41 (1965)(Russ). Absorption, fluorescence, and phosphorescence spectra were detd. for Zn mesoporphyrin, Zn tetrabenzoporphyrin, and Cu mesoporphyrin. Polarization of phosphorescence of the investigated compds. was 1/7 and was independent of wavelength of the exciting light. In metal porphyrins, the oscillator of phosphorescence is in the plane of the mols.

Gurinovich, I. F., Gurinovich, G. P.,　　　　1, 2, 13
and Sevchenko , A. N.　　　　　　　　　　CA 61-1868d (1964)

The structure of products of photochemical reactions of porphyrins. Dokl. Akad. Nauk SSSR 155 (6), 1345-7 (1964). Ultraviolet and infrared spectra of tetraazoporphyrin were taken and a comparison was made between those taken after redn. with H_2S in pyridine and after contact with air. Photoredn. gave a product with an absorption band at 450 mμ, which disappeared after air oxidn. The infrared spectrum of the reduced product contained new bands at 615, 1280, 1380, and 1460 cm.$^{-1}$ with disappearance or weakening of bands at 635, 803, 1340, 1510, and 1558 cm.$^{-1}$ Absorption in the 2800-3000 cm.$^{-1}$ region increased after redn., while the 3085 and 3300 cm.$^{-1}$ bands vanished. The results indicated that the photoredn. did not involve addn. of H atoms to the bridge N atoms, but probably did involve the pyrrole rings.

Gurinovich, I. F. and Gurinovich, G. P.   2, 14
                                                       CA 59-14737c (1963)

Infrared spectra of porphyrins. Optika i Spektroskopiya, Akad. Nauk
SSSR, Otd. Fiz.-Mat. Nauk, Sb. Statei 2, 196-205 (1963). The infrared
spectra of a series of porphyrin derivs. were measured and compared
in KBr or in soln., including pyrrole, bilirubin, protoporphyrin,
mesoporphyrin, Mg mesoporphyrin, tetraphenylporphine, Mg tetraphenyl-
porphine, tetraazaporphine, and Mg phthalocyanine. The changes in the
spectra and the shifts of the bands during the transition from pyrrole
to porphyrin are discussed. Some rules are given. The effects of
conjugated systems and of the formation of a big vibrating system, and
esp. of the participation of the benzene ring are discussed. The
characteristics of the vibrations of the NH group are derived.

Gurinovich, G. P., Sevchenko , A. N.   1, 2
and Solov'ev, K. N.   CA 58-13300d (1963)

Spectroscopy of the porphyrins. Usp. Fiz. Nauk 79, 173-234 (1963).
A review with 193 references.

Gurinovich, G. P., Shul'ga, A. M.   2, 15
and Sevchenko , A. N.   CA 60-8269b (1964)

Polarized luminescence of reduced forms of porphyrins. Dokl. Akad.
Nauk SSSR 153 (3), 703-5 (1963). Protoporphyrin and tetraphenyl-
porphine in EtOH-pyridine were subjected to photoredn. in the presence
of ascorbic acid at liquid air temp. and found to produce some 40-5%
polarized luminescence spectra in regions of 730 and 810 mμ. Such
high levels of polarization indicated a low order of symmetry of both
types of redn. products; these cannot be represented by formulas with
localized H atoms on both central N atoms. The literature on redn.
products of porphyrins is reviewed.

Gurinovich, G. P.   15, 13, 1, 18, 17, 4
                                                       CA 55-26661c (1961)

Luminescence of dyes of the porphine series. Trudy Inst. Fiz. i Mat.,
Akad. Nauk Belorus. S.S.R. 1959, No. 3, 111-30. A study was made of
the absorption and polarization spectra of the fluorescence of
chlorophyll a, chlorophyllide a, Mg phthalocyanine, and protoporphyrin
in a mixt. of glycerol-cyclohexanol and glycerol-EtOH and in cyclohexanol.
Most of the polarization detns. were made on a photoelec. polarimeter.
All of the objects studied have pos. fluorescence polarization. The
absorption and emission of chlorophyll in the 405 and 660 mμ bands had

a dipole character; consequently, the results of the polarization measurements were converted to excitation by polarized light according to the Levshin-Vavilov formula. A dependence was found between the degree of polarization and the wavelength of emission and absorption of 3-monomethylaminophthalimide. The max. degree of polarization corresponded to a pure electron transition, which agrees with the law of mirror symmetry. A similar result was obtained for fluorescein and Rhodamine B. The degree of fluorescence polarization of protoporphyrin had a max. in the short-wave band and was practically zero in the long-wave band; the same is the case for Mg phthalocyanine. This sharp difference in the degree of polarization is due to the participation of several electron levels in emission. For this group of compds. a decrease in the quantum yield of fluorescence with the increase in the viscosity of the medium was observed; this is due to a quenching of the 1st order (chem) since the av. duration of the excited state remains const. while the viscosity varies. From Referat. Zhur., Fiz. 1960, Abstr. No. 12508.

Hagenbach, A., Auerbach, F., and   1, 2, 13
Wiedemann, E.   CA 30-2490 (1936)

Light absorption and constitution of porphyrin dyes. Helv. Phys. Acta 9, 3-26 (1936). The change of absorption spectra of porphyrins was studied in relation to changes in the skeleton structure of the porphyrin nucleus, covering the wavelength range 650-300 mμ. Ether with addn. of pyridine was used as solvent. The molar coeff. of extinction and the absorption max. of the following compds. are stated and absorption curves given: phylloporphyrin, rodoporphyrin, pheoporphyrin, dihydropheophorbide a, hemochromogen, pheophorbide a, pheophorbide b, chlorophyll a and chlorophyll b.

Harris, R. L. N., Johnson, A. W.   .   2, 11, 12
and Kay, I. T.   .   .   CA 63-7014a (1965)

Stepwise synthesis of porphyrins and related macrocycles from 1, 19-dideoxy-ac-biladienes. (Univ. Nottingham, Engl.). Chem. Commun. 1965 (11), 232-4 (Eng).

Haurowitz, Felix, Kraus, F., and Appel, G.   1, 15, 2
                                                  CA 32-7343 (1938)

Porphyrins and their metal salts.   V.   Absorption and fluorescence of
porphyrins in various solvents and the fine structure of the porphyrin
ring.   Ber. 71B, 1404-12 (1938); cf. C.A. 30, 2060^3.   Absorption max,
were obtained for tetramethylhemato- and dimethylmesoporphyrin in 30
different org. solvents and in 6 acid solns.   The solns. were examd.
for fluorescence with the ultraviolet Hg spectrum.   Transference
measurements on etioporphyrin-III in HCl-MeOH soln. show cathodic
migration of the coloring matter.

Haxo, Francis T.   13
                                                  CA 55-4597f (1961)

Wavelength dependence of photosynthesis and the role of accessory
pigments.   (Scripps Inst. of Oceanography, La Jolla, Calif.).   Ibid.
339-60.   Comparative Biochemistry of Photoreactive Systems (V.1 of
Symposia on Comparative Biology) Mary Belle Allen Ed., New York,
Academic Press, 1960.

Hazato, G.   10, 2
                                                  CA 61-2597d (1964)

Simple molecular orbital study on the ring current model of the
porphine skeleton.   (Tohoku Univ., Sendai, Japan).   Proc. Intern. Symp.
Mol. Struct. Spectry., Tokyo 1962 (D217), 4pp. (in English).   Evaluation
of the ring current shifts were made with the London-type M.O. method,
including the Coulomb integral for the N atoms.   Correlation of the
ring current shift of the ring proton with δN, the Coulomb integral
correction for the N atom, is presented graphically.   It is noted that,
unlike C_5H_5N or C_4H_5N, the total sum of ΔK_i increases greatly with
increasing δN.   This trend is reflected in the net shifts for N-H pro-
tons, requiring large neg. corrections to adjust them to the exptl.
values.

Heilmeier, G. H. and Harrison, S. E.   4, 13
                                                  CA 59-7065b (1963)

Implications of the intensity dependence of photoconductivity in metal-
free phthalocyanine crystals.   (RCA Labs., Princeton, N. J.).   J. Appl.
Phys. 34 (9), 2732-5 (1963).   The evaluation of phthalocyanine as a
photoconductive material has led to the unusual result that the photo-
current varies as the one-third power of the light intensity.   This
effective desensitization is analyzed in terms of diffusion effects
involving the surface.

Heilmeier, G. H., and
Warfield, George

1, 4,
CA58-6329a (1963)

Optical absorption spectrum of metal-free phthalocyanine single crystals. (Princeton Univ., Princeton, N. J.). J. Chem. Phys. 38, 893-7 (1963). The optical absorption spectrum of the mol. crystal metal-free phthalocyanine was investigated, 25,000-3500 A. The spectrum of the phthalocyanine mol. retains much of its identity in the crystal, as evidenced by the similarity in the regions of main absorption. This is a consequence of the weak intermol. binding forces. The crystal absorptions in the region 8000-5000A., and below 4000 A. can be attributed to excitations from the highest filled M.O. to the vibrationally broadened and shifted excited states of the mol. which occur in the crystal field. Vibrational structure was observed which was attributed to a sym. breathing vibration of the peripheral benzene rings and, quite possibly, a similar vibration of the entire phthalocyanine mol.

Hellström, Harry

1, 2
CA 30-5124 (1936)

Relation between constitution and spectra of porphyrins. A level-system of porphyrin molecules. Arkiv Kemi, Mineral. Geol. 12B, No. 13, 6 pp. (1936); cf. C. A. 27, 3141. The absorption bands of porphyrins have been classified according to energy levels. The corresponding fluorescent bands have been observed and calcd. Band systems belonging to the pyrrole and pyrrolene nuclei and isocyclic rings are indicated. The fluorescent spectra of deuteroporphyrin, etioporphyrin and desoxophylloerythrin in ether and the absorption bands of mesoporphyrin are given.

Hershenson, H. M.

1
CA 65-13056c (1966)

Index for 1960-1963 (Ultraviolet and Visible Absorption Spectra, Vol. 3). New York: Academic. 1966. 223 pp. $14.

Evidence for porphyrins in the Orgueil meteorite. (Res. Council
Alberta, Edmonton, Can.). Nature 202 (4928), 125-31 (1964). Org.
matter extd. from 6 samples representing 4 stones of the Orgueil
carbonaceous meteorite was subjected to a series of spectral, chromato-
graphic, and chem. tests which reveal the presence of pigments indistin-
guishable from esterified vanadyl porphyrins of terrestrial ancient
sediments and petroleum. The pigments were present either because they
were indigenous, or because the stones became contaminated with pigment-
bearing substances. Limited data available for possible contaminants
such as dusts, soils, and recent sediments show that these substances
contain both chlorins and porphyrins, with the chlorins in marked
excess over the porphyrins. The virtual absence of chlorins in the
meteorite exts., therefore, does not support the contamination possi-
bility. Vanadyl porphyrins are evidently indigenous to ancient
terrestrial carbonaceous rocks arising out of sediments deposited under
reducing conditions replete with biogenic activity. The Orgueil
carbonaceous chrondrite exhibits many of the org. components of
ancient terrestrial rocks, and an earlier detailed consideration of
the environment of the Orgueil meteorite parent body led to the indi-
cation that the environment was a low-temp. aq. system with an alk.
pH and slightly reducing oxidn.-redn. potential. What presently
appear to be indigenous porphyrin pigments in the Orgueil stones
strongly suggest a possibility of biogenic agencies in the origin of
the org. matter of the Orgueil meteorite.

Hoffman, Donald R.   16, 13, 2
                                                          CA 63-14673c (1965)

Mass spectra of porphyrins and chlorins. (Harvard Univ.). J. Org.
Chem. 30 (10), 3512-16 (1965)(Eng). The mass spectra of several
porphyrins and chlorins of synthetic and biological interest have
been obtained and interpreted. These compounds fragment only
peripherally as one would expect of a large aromatic system. Sub-
stituents in the 7- and 8-positions in chlorins are more labile than
pyrrole ring substituents. γ-Substituents are even more labile and
are lost with the transfer of one and two hydrogens to the tetra-
pyrrole system, if possible. A steric effect is observed in the loss
of γ-substituents. The spectra of compounds containing additional
five- and six-membered carbocyclic rings, including methyl phaephorbide,
were obtained and interpreted. The directions of ring closure predicted
for two isomeric chlorins in Woodward's chlorophyll synthesis were con-
firmed. The mass spectra of several compounds containing six-membered
lactone rings are discussed. Mechanisms are proposed for several of
the types of fragmentations observed.

Holt, A. S. and Jacobs, E. E.   17, 14

Infra-Red absorption spectra of chlorophylls and derivatives. Plant
Physiology 30 (1955) p. 553.

Holt, A. S.   17, 14
                                                          CA 59-10386a (1963)

Infrared spectroscopy of chlorophylls. (Natl. Res. Council, Ottawa,
Can.). Proc. Intern. Congr. Biochem., 5th, Moscow, 1961, 6, 59-63
(Pub. 1963). Infrared spectra of chlorophylls are studied in order to
det. groupings involved in reversible in vitro reactions. Derivs.
of chlorophyll a in nonpolar solvents have absorption bands at 1610
cm.$^{-1}$ which, by comparison with related compds., are not due to C-2
vinyl or aromatic C=C bonds but to charge distributed on both ketone
and ester carbonyls as well as on C-10. The 1645 cm.$^{-1}$ band appears
only with Zn and Mg derivs. and is also dependent on the presence of
the C-9-keto group in the isocyclic ring which enolizes.

Holt, A. S.   17, 11
                                                          CA 63-13616h (1965)

Nature, properties, and distribution of chlorophylls. (Natl. Res.
Council, Ottawa, Can.). Chem. Biochem. Plant Pigments (T. W. Goodwin,
editor. Academic) 1965, 3-28 (Eng). 186 references.

Holt, A. S. and Morley, H. V.   17, 13, 11
CA 55-4597d (1961)

Recent studies of chlorophyll chemistry. (Natl. Research Council, Ottawa, Can.). Ibid. 169-79. Comparative Biochemistry of Photo-reactive Systems (V.1 Symposia on Comparative Biology) Mary Belle Allen, ed., New York Academic Press, 1960.

Holt, A. S. & Morley, H. V.   17, 11
CA 53-16148b (1959)

Proposed structure for chlorophyll d. (Natl. Research Council, Ottawa). Can. J. Chem. 37, 507-14 (1959).

Horie, Shigeo and Morrison, Martin   5, 1
CA 59-4207a (1963)

Cytochrome c oxidase components. III. Spectral properties of cytochromes a and a_3. (City of Hope Med. Center, Duarte, Calif.). J. Biol. Chem. 238 (8), 2859-65 (1963); cf. CA 58, 14392c. The spectral properties of a purified cytochrome c oxidase prepn. were investigated. A procedure is outlined by which the difference spectra of any desired combination of reduced and oxidized cytochromes a and a_3 can be obtained. The reduced vs. oxidized difference spectrum of cytochrome a_3 and the difference spectrum of oxidized vs. reduced CO-cytochrome a_3 are presented. The procedure can be modified to obtain abs. spectra of the cytochrome c oxidase prepn. in which cytochromes a and a_3 are present in different valence states. Thus, spectra are shown of the prepn. with either oxidized cytochrome a and reduced cytochrome a_3 or, conversely, reduced cytochrome a and oxidized cytochrome a_3. It is also possible to obtain the spectrum of the prepn. equiv. to partially reduced cytochrome a_3 in the presence of oxidized cytochrome a or, conversely, the equivalent of partially reduced cytochrome a in the presence of oxidized cytochrome a_3. Examples are also given of the spectra of various combinations of partially reduced cytochromes a and a_3. It is noted that most of the previous speculations concerning the contributions of the 2 cytochromes to the absorption at 444 and 605 mμ in the reduced form are questionable. The most significant point in this regard is the high contribution of cytochrome a to the Soret peak of the reduced cytochrome c oxidase prepn. Cytochrome a accounts for at least twice as much of the absorption at 444 mμ as does cytochrome a_3.

Ingram, D. J. E.   16
                                                    CA 53-882d (1959)

Free Radicals as Studied by Electron Spin Resonance.   New York:
Academic Press. 1958.   274 pp. $9.50.

Ingram, D. J. E., Bennett, J. E., George, P. & Goldstein, J. M.
                                        16, 4, 2
                                        CA 50-13606e (1956)

The paramagnetic resonance spectra of copper porphine derivatives.
(Univ. of Pennsylvania, Philadelphia).   J. Am. Chem. Soc. 78, 3545-6
(1956); cf. C.A. 49, 5122h; preceding abstr.--The paramagnetic res-
onance absorption spectra of the Cu complexes of α, β, γ, δ-tetra-
phenylporphyrin and its p-Cl deriv.   (Rothemond and Menotti, C. A.
42, 6357g), was investigated.   Dipole-dipole interaction between
neighboring Cu atoms in such large mols. is so reduced, even in the
concd. crystal, that the separate hyperfine components of the spectrum
can be resolved without resorting to diln. with an isomorphous
diamagnetic compd.   The hyperfine structure of the unchlorinated
deriv. consists of 4 equally spaced components as in most Cu compds.,
and the values are very close to those obtained for Cu phthalocyanine
(loc. cit.).   The hyperfine pattern of the Cl deriv. shows that there
is considerable interaction with the Cl nuclei which causes a further
splitting of each hyperfine component.   Since the splitting is so
large (about 100 gausses), it implies that the magnetic electron is
assocd. with the Cl atoms for an appreciable time.   The estd. interat.
Cl-Cu distance in this particular mol. is about 9-10 A.   Although such
a long-range interaction is well-known for free radicals, it has not
been previously observed for the case of magnetic electrons assocd.
with a normal paramagnetic atom.

Ingram, D. J. E., Kendrew, J. C.   9, 11
                                                    CA 51-4455b (1957)

Orientation of the hem group in myoglobin and its relation to the
polypeptide chain direction.   (Univ. Southhampton, Engl.).   Nature
178, 905-6 (1956); cf. C.A. 50, 7583g.--Electron spin resonance
measurements on myoglobin were satisfactorily correlated with optical
measurements of the dichroic ratio and with indications of the pre-
dominant polypeptide chain directions derived from Patterson syntheses
computed from x-ray diffraction data.

Ingram, D. J. E. & Bennett, J. E.   16, 4, 9
                                     CA 50-10839b (1956)

Paramagnetic resonance in phthalocyanine, hemoglobin, and other organic
derivatives. (Univ. Southampton, Engl.). Discussions Faraday Soc.
No. 19, 140-6 (1955).--Exptl. work on these compds. is difficult because
of the small size of the crystals available. By using 8-mm. and 1.25-cm.
wavelengths and small resonant cavities, small crystals could be examd.
g-Values were obtained for Cu, Fe, and Co metallic derivs. of phthalocya-
nine and indicated differences from the expected ionically bound bi-
valent values. Four Cu derivs. of chlorophyll showed a single line.
Measurements on hemin, acid-met-ferrihemoglobin, acid-met-ferrimyoglobin,
ferrihemoglobin fluoride, and ferrimyoglobin fluoride indicate that the
binding to the Fe atom is not "essentially ionic" and the structure is
different from that previously assumed. Measurements on ferrihemoglobin
and ferrimyoglobin azide confirm the essentially covalent bonding pre-
viously supposed.

Ingram, D. J. E. & Bennett, J. E.   16, 17, 9, 4
                                     CA 48-11921g (1954)

Paramagnetic resonance in phthalocyanine, chlorophyll, and hemoglobin
derivatives. (Univ. Southampton, Engl.). J. Chem. Phys. 22, 1136-7
(1954).--Preliminary measurements of the paramagnetic resonance absorp-
tion were summarized for crystals of the following compds.: Cu
phthalocyanine, Co phthalocyanine, Fe phthalocyanine, Mn phthalocyanine,
V phthalocyanine, Ni phthalocyanine, 4 Cu chlorophylls, and hemoglobin.

Inhoffen, H. H., Bliesener, C., & Brockmann, H. Jr.
                                     CA 65-18589a (1966)

Chlorophyll and hemin, VIII, Transformation of protoporphyrin IX via
photoprotoporphyrin into spirographis- and isospirographisporphyrin.
(Tech. Hochsch., Brunswick, Ger.). Tetrahedron Letters 1966(31),
3779-83(Ger).

Ionaitis, G. and Kazlauskene, A.   1, 3
                                     CA 59-10898d (1963)

Temperature effect on the electronic absorption spectra of carotene.
(V. Katukas State Univ., Vilnyus). Fiz. Probl. Spektroskopii, Akad.
Nauk SSSR, Materialy 13-go [Trinadtsatogo] Soveshch., Leningrad, 1960,
1, 294-5(Pub. 1962). The absorption spectra of the mixt. of α-, β-,
and γ-carotene were investigated at different temps. They were taken
in visible and ultraviolet light from $+20^\circ$ to -196° in EtOH, Et_2O, mixt.
of both (1:1), and petr. ether. The visible absorption spectrum of the

carotene mixt. as well as of α- and β- carotene is shifted at low temps. to the long wavelength side owing to the transfer of a greater no. of mols. in the trans form. The temp. dependence of the absorption max. is straight-lined. The stereoisomerization of carotenes produced new absorption max. between 3300 and 3400 A. (cis peak). Between 3200 and 4000 A., 3 max. were obtained in the mixt. of α- and β-carotene in petr. ether: only 1 was identical with the cis peak (3305 A.). In ultraviolet light, the general absorption increased at low temps., but less than in the visible. The addnl. max. in the ultraviolet is not a result of the stereoisomerization of carotene. At low temp., the majority of the carotene mols. go into the trans form and the intensity of the absorption spectrum in the ultraviolet region has to decrease. The max. in the ultraviolet occurred only in the solns. of α-carotene.

Isler, O.   13
                                                   CA 52-17615f (1958)

Vitamin A and carotinoids. (Hoffmann-LaRoche, Basel, Switz.). Angew. Chem. 68, 547-53 (1956).--A review of the work of I., et al. 12 references.

Ivanov, N. P. and Il'ich, G. K.   1, 13
                                                   CA 57-4195d (1962)

Spectral characteristics of vitamins B_1 and B_2. (Phys. Inst., Minsk). Lab. Delo 8, No. 2, 24-7 (1962). Absorption and luminescence characteristics of riboflavin (I), thiamine (II), and thiochrome (III) were studied at various pH values. II had absorption max. at 234 and 267 mμ at pH 7.0, 8.7, and 9.7, and absorbancy at these wavelengths increased with increase in pH. Absorption max. of II were at 247 and 257 mμ at both pH 3 and 5, and absorbancy at these wavelengths increased with decrease in pH. III had a luminescence max. at 450 mμ, and its intensity decreased markedly with increased periods of irradiation. All absorption max. of I, except that at 445 mμ, underwent a very small shift toward the ultraviolet, while the absorption max. at 445 mμ shifted to 400 mμ as pH was brought from 7 to 11. At pH 0.7 absorbancy of I at 445 mμ decreased, while other spectral properties of I remained virtually the same. I fluoresced with a max. at 545 mμ and the intensity of luminescence was decreased in both strongly acidic and basic solns. Although the intensity of luminescence of I decreased as a result of prolonged irradiation, the change was much smaller than that of III.

Jackson, A. H., Budzikiewicz, H., Djerassi,   7, 13, 16
Carl, Kenner, G. W., Smith, K. M. and   CA 64-3325d (1966)
Aplin, R. T.

Mass spectrometry in structural and stereochemical problems. LXXVI.
Pyrroles and related compounds. 8. Mass spectra of porphyrins. (Univ.
Liverpool, Engl.). Tetrahedron 21 (10), 2913-24 (1965)(Eng); cf. CA
62, 13150d; 63, 11477a, 16183e, 18188f. The mol. ion nearly always
produces the strongest peak in mass spectra of porphyrins. The macro-
cyclic nucleus is remarkably stable and fragmentation gives mainly
benzylic ions. In derivs. of porphyrin this involves cleavage at the
bond once removed from the macrocycle, but in chlorines the entire
substituent is lost from the reduced pyrrole ring. Me esters of
chlorines derived from chlorophyll lose directly 147 and 159 mass units
in complex processes marked by strong metastable peaks. All the spectra
contain a prominent series of peaks from doubly charged ions; a novel
feature is loss of ketene from propionate side chains.

Jacobs, E. E. et al   1, 17, 13
                                                  CA 52-3522f (1958)

Spectroscopic properties of crystals and unilayers of chlorophyll and
related compounds. (Univ. of Illinois, Urbana). Arch. Biochem.
Biophys. 72, 495-511 (1957); cf. C.A. 48, 4603i; 51, 4505i.--Micro-
crystals of Et chlorophyllides and pheophorbides a and b, and of Me
bacteriochlorophyllide, were prepd. and their absorption spectra detd.
The main long-wave bands are shifted toward longer waves by $1-2 \times 10^3$
cm.$^{-1}$ compared with their (extrapolated) position in free mols. (i.e.
by 40-80 mμ from their position in org. solvents). The shift is a
function of the size of the microcrystals, reaching satn. in crystals
about 0.5 μ in diam. An only slightly smaller shift is observed in
cryst. unilayers; this condition indicates that the interactions re-
sponsible for the shift occur mainly in 1 crystallographic plane. In
liquid unilayers, the shift is much smaller, similar to that in amor-
phous colloid solns. A theory of the band shift is given; it is based
on electrostatic interaction in an isotropic array of (virtual) dipoles,
created by light absorption (without consideration of the overlapping
of eigenfunctions and consequent resonance effects). The abs. value
of the max. shift in large microcrystals, and, in particular, the
shape of the curve showing the dependence of the shift on crystal size,
support the assumption of a predominantly 2-dimensional interaction.
The significance of these results for the hypothetical chlorophyll
unilayers in vitro and the possible migration of excitation energy in
them is discussed. Absence of fluorescence suggests that migration
must be very restricted, if at all existent, in crystals and cryst. uni-
layers; it could be more extensive in noncryst. unilayers. The existence
of unilayers of the latter type is compatible with the absorption spectrum
of chlorophyll in vivo.

Jaffe, H. H. & Orchin, Milton   CA 58-4070f (1963)

Theory and Applications of Ultraviolet Spectroscopy. New York: John
Wiley and Sons. 1962. 624 pp.

Jannelli, Liliana, and Orsini, P. G.   7, 13
                                                  CA 58-12003f (1963)

The system pyrrole-benzene. Cryoscopic behavior. Rend. Accad. Sci.
Fis. Mat. (Soc. Nazl. Sci., Napoli)[4]26, 246-50 (1959). F.ps. were
measured for the system pyrrole-benzene at concns. from 0 (pure benzene)
to 1 (pure pyrrole). From these the state diagram was obtained, and
the eutectic temp.(-36.6°) and compn. (0.774) were calcd. The m.p. of
pure pyrrole is 23.54°. The activity coeff. of the pyrrole increases
with increasing pyrrole concn. This is attributed to (1) dimeric
assocns. of pyrrole, and (2) deviation of the system from ideality
due to solute solvent interaction.

Jennings, A. L., and Boggs, J. E.   13, 16
                                                  CA 61-9382f (1964)

Mass spectrometry for structure determination. Simple nitrogen hetero-
cycles. (Univ. of Texas, Austin). J. Org. Chem. 29(7), 2065-6 (1964).
The mass spectra of 20 simple N heterocyclic compds. were measured on
a modified Consolidated Engineering Corp. mass spectrometer model
21-102, and the complete spectra submitted for distribution. The
relative intensities of N_2^+, CNH_2^+, $C_3H_3^+$, M-HCN, M-C_3H_3, M-C_2H_4O
fragments were listed in % of base peak. More than 5% m/e 28 was
present in all spectra except that of 2-methylcarbazole. With the
exception of N_2^+ mols. CNH_2^+ appears to be the main contributor. Ac-
cordingly absence of m/e 28 would eliminate the possibility of adjacent
N atoms in a given N heterocyclic compd. and of a unsubstituted ring
N atom between 2 C atoms with 2 H atoms attached to the C-N structure.
A peak at m/e 39 appeared wherever there were 3 or more C atoms in a
chain with at least 3 H atoms among them. The non-appearance of a
significant m/e of 39 indicates the absence of such a chain. It was
further concluded that no Ac group is present on a given N hetero-
cyclic ring if a significant parent ion minus 43 m/e peak is not present
in the spectrum.

Jensen, Synnove Liaaen   3, 11

Carotenoids of Photosynthetic Bacteria - Distribution, Structure and
Biosynthesis Part I. Bacterial Photosynthesis, Howard Gest, Anthony
San Pietro and Leo P. Vernon (ed.)

Johnson, A. W.

2, 11

CA 50-12025d (1956)

Recent advances in science: Organic chemistry. (Univ. Nottingham,
Engl.) Science Progr. 44, 499-506 (1956) A review of recent researches
on the biogenesis of the porphyrins.

Johnson, A. W.

11, 13

CA 50-12973g (1956)

Recent advances in science: Organic chemistry. (Univ. Nottingham,
Engl.) Science Progr. 44, 81-8 (1956). A review of recent investi-
gations on vitamin B_{12}.

Jonaitis, H., Kazlauskiene, A., and
Rukstelyte, E.

1, 3

CA 55-16136g (1961)

Effect of low temperatures on the ultraviolet absorption spectrum of
carotene. Vilniaus Univ., Mokslo Darbai 33, 113-15 (1960)(Russian
summary, 115).--Absorption max. at 3305, 3487, and 3700 A. at 18° were
observed in the ultraviolet spectrum of α- and β-carotene mixt. in
petr. ether soln. Decrease of temp. to -196° caused the max. to shift
towards the longer wave-length side at a rate of 0.25 A./°C. Absorp-
tion intensity increased with decreasing temp.

Jonaitis, H., et al

1, 3

CA 55-16136i (1961)

Effect of temperature on visible light absorption spectrum of carotene.
Vilniaus Univ., Mokslo Darbai 33, 117-23 (1960)(Russian summary, 122).
--Spectra of α- and β-carotene mixt. in petr. ether, EtOH, Et_2O, and
octane solns. were investigated between 18 and -196°. Absorption max.
at 4760 and 4460 A. were observed at 18°. The 3rd max. at 4240 A. was
noticed at temp. below -78°. Absorption intensity increased with
decreasing temp., and max. were shifted towards the longer wave-length
side at a rate of 0.72 A./°C. The shift rate was linear with respect
to temp., except at the solvent m.p. Phys. properties of solvents had
only slight effect on absorption spectra. Split of peaks was observed
with nonpolar solvents.

7129-Final   150

Jonaitis, H., Kadunaite, D.
and Kazlauskiene, A.

1, 3
CA 59-14389c (1963)

Effect of temperature and solvent on the electron absorption spectrum
of β-carotene. Lietuvos Fiz. Rinkinys. Lietuvos TSR Mokslu Akad.,
Lietuvos TSR Aukstosios Mokyklos 2 (3-4), 415-21 (1962)(in Russian).
The absorption spectra of synthetic β-carotene were measured, +20 to
-196°, in soln. in n-hexane, n-heptane, n-octane, n-nonane, toluene,
PrOH, CHCl$_3$, PhCl, and benzene. The 3 absorption max. in the visible
range shifted to longer wavelength with decreasing temp. The wave-
lengths of the max. depended on the nature of the solvent. They were
a function of $f(n) = (2n^2 - 2)/2n^2 + 1)$. The interaction of the solute
mol. with the solvent mols. is discussed.

Jonaitis, H., Kazlauskiene, A.
and Salna, V.

1, 3
CA 64-12046h (1966)

Effect of the solvent on the electronic spectra of vitamin A and
β-carotin. Tr. Komis. po Spektroskopii, Akad. Nauk SSSR 3 (1), 664-72
(1964)(Russ). The effect of the solvent on the position, intensity,
and magnitude of the temp. shift in absorption bands of solns. of
vitamin A and β-carotin in the uv and visible spectrum was studied.
The magnitude of spectrum shifts was dependent on the phys. properties
of the solvent. From Ref. Zh., Fiz., D. 1965, Abstr. No. 12D300.

Jonaitis, H. and Krisciuniene, B.

1
CA 59-13485d (1963)

Dependence of the absorption spectra of vitamins B$_1$ and C on tempera-
ture. Lietuvos Fiz. Rinkinys, Lietuvos TSR Mokslu Akad., Lietuvos
TSR Aukstosios Mokyklos 2 (3-4), 409-14 (1962)(in Russian). The
ultraviolet absorption spectra of alc. solns. of vitamins B$_1$ and C
were measured, +20 to -150°, by a spectrometer and a special thermo-
stat. When the temp. decreased, the absorption max. were raised and
shifted to longer wavelength at concns. of 10^{-4} g/cc. The effects
depended on the concns. In aq. solns., there was no change up to the
point of congealation. The effects were explained by an alteration of
the probability of electron-vibrational transitions.

Jonaitis, H., Kazlauskiene, A.   1, 13
and Salna, V.   CA 59-13485a (1963)

Effect of the solvent on the absorption spectrum of vitamin A.
Lietuvos Fiz. Rinkinys, Lietuvos TSR Mokslu Akad., Lietuvos TSR
Aukstosios Mokyklos 2 (3-4), 401-7 (1962). The shift of the 300-mμ
absorption max. of vitamin A was investigated spectrophotometrically
in the following solvents: EtOH, PrOH, iso-BuOH, n-hexane, n-heptane,
n-octane, n-nonane, benzene, toluene, $CHCl_3$, PhCl, CCl_4, Et_2O, PrOAc,
iso-PrOAc, and benzene. The shift depended on the $n(n^2 - 1)/(2n^2 + 1)$
and on the dielec. const., ε, but it could not be explained by these
macroscopic properties alone. The height of the max. was also depen-
dent on the solvent.

Jones, R. A.   1, 14, 7
                                     CA 58-13315g (1963)

Pyrrole studies. I. Infrared spectra of 2-monosubstituted pyrroles.
(Univ. Adelaide). Australian J. Chem. 16, No. 1, 93-100 (1963). The
positions and intensities of the characteristic infrared absorption
bands of the nucleus were obtained for 35 2-monosubstituted pyrroles
in the region 2000-800 cm^{-1}.

Kamen, Martin D.   9, 12

The Heme Proteins of Photosynthetic Bacteria. Bacterial Photosynthesis -
Howard Gest, Anthony San Pietro, and Leo P. Vernon (ed.).

Kamen, Martin D.   9, 12
                                                    CA 59-7858a (1963)

.The heme proteins of photosynthetic tissues. (Brandeis Univ., Waltham,
Mass.). Proc. Intern. Congr. Biochem., 5th, Moscow, 1961, 6, 242-50
(Pub. 1963)(in English). A review with 47 references on the occurrence
and nature of heme proteins in plants, photosynthetic bacteria, and on
photosynthesis and enzymes assocd. with photosynthetic heme proteins.

Kamen, Martin D.   12
                                                    CA 60-870a (1964)

Advanced Biochemistry. Vol. 1. Primary Processes of Photosynthesis.
New York: Academic Press. 1963. 182 pp.

Kamen, Martin D.   9, 12
                                                    CA 55-4597f (1961)

Hematin compounds in photosynthesis. (Brandeis Univ., Waltham, Mass.).
Ibid. 323-37. Comparative Biochemistry of Photoreactive Systems (V.1
of Symposia on Comparative Biology) Mary Belle Allen, ed., New York,
Academic Press, 1960.

Karapetyan, N., Litvin, F. F.   17, 1
and Krasnovskii, A. A.   CA 58-14443e (1963)

Investigation of the phototransformations of chlorophyll by differential
spectrophotometry. (A. N. Bakh Inst. Biochem., Moscow). Biofizika 8,
191-200 (1963); cf. CA 53, 2375c. The app. permitted the measurement of
the differential light-darkness spectra of solns. of chlorophyll (I).
The differential absorption spectra of I measured in solns. were very
similar when I was being photoreduced and photooxidized. During the
reversible photoredn. of I, both slower changes and rapid (less than
one sec.) completely reversible stages occur. During photooxidn., slow,
irreversible changes of I occur. In the differential spectra of suspen-
sions of the green alga Chlorella pyrenoidosa, the changes in the red
region during illumination were chiefly due to a change in the fluores-
cence, while a change of absorption was observed in the green region of
the spectrum. The position of the long wave max. of suspensions of the

photosynthetic bacteria Chromatium and Rhodopseudomonas palustris c.-
pends on the age of the culture. Under the action of intense light
impulses, the change of the luminescence of chlorophyll stimulated by
monochromatic measuring light should be considered in interpreting
the differential light spectra.

Karpitskaya, V. and Dilung, I. I.   17, 1, 11
                                                CA 60-4384b (1964)

Photochemical oxidation of chlorophyll in frozen solutions.   Dokl.
Akad. Nauk SSSR 152 (2), 367-9 (1963). The complexing of chlorophyll
(I) with O_2 was studied in the solid state in alc., C_6H_6, $C_6H_5CH_3$,
$CHCl_3$, and CCl_4 or mixts. of these solvents. Irradiations employed
red light from a filament lamp. In one expt. (alc. soln.) O_2 was ad-
mitted, the frozen glass photolyzed and new peaks appeared at 465,
490, 520, and 580 mμ; this was taken as evidence of dehydration at
C-7 and C-8 in the pyrrole ring. Because of restricted mol. motion
at 77°K it is proposed that a mol. complex between I and O_2 is respon-
sible for the oxidn. The dark reaction of O_2 with I was studied spec-
trally; degassed solns. of I in C_6H_6 show a 10-20% increase in optical
absorption at 680 and 425 mμ when O_2 is admitted at several atms.
Similar studies in alc. give the same spectral changes, but require a
longer time. It is concluded that I enters into a dark reaction
(complexing) with O_2.

Karrer, Paul and Jucker, Ernst   3
                                                CA 45-3892g (1951)

  ...noids. New York: Elsvier Pub. Co. 1950. 384 pp. Sommerhoff,
G.: Analytical Biology. New York: Oxford Univ. Press. 1950. 207 pp.

Karyakin, A. and Chibisov, A. K.   1, 17
                                                CA 58-2024h (1963)

Spectral investigation of water state in chlorophyll. (V.I. Vernadskii
Inst. Geokhim. and Anal. Chem., Moscow). Biofizika 7, 561-7 (1962).
The infrared and visible absorption spectra of hard films and solns. of
chlorophyll, as well as the fluorescence spectra of solns. of the pig-
ments, were investigated. The H_2O bound in chlorophylls a and b had
different bond strengths and, accordingly, different rates of isotopic
exchange with D_2O. It was assumed that at the place of interaction of
chlorophyll a with H_2O the atoms of O of the cyclopentanic ring appear.
The H_2O bound with the pigments had a strong effect on the electronic
absorption and emission spectra of chlorophyll.

Kato, Sechi, Tonomura, Shizu
and Yamamoto, Kazuko

1, 17
CA 47-11981h (1953)

Spectroscopic nature of chlorophyll. J. Sci. Research Inst. (Tokyo)
46, 118-25 (1952). On the basis of previously published data in the
literature, especially the data concerning the absorption and fluores-
cence spectrum of chlorophyll-type compds. (I), in the visible range
the following conclusions are drawn. The first strong and second weak
absorption given by I is attributed to the transition taking place
between the vibrational excited state (one step) of the ground state
and nonvibrational state of the next higher energy level. The mol.
is mostly in the vibrational excited state at room temp. owing to the
symmetry of the electric field caused by the hydrogenation of one of
the nuclei. The fluorescence is attributed to the transition taking
place between the antisymmetrical vibrational state of the ground
state and the nonvibrational state of the next higher energy level.

Katz, J. J., Closs, G. L., Pennington,
F. C., Thomas, M. R., and Strain, H. H.

14, 17
CA 60-1238h (1964)

Infrared spectra, molecular weights, and molecular association of
chlorophylls a and b, methyl chlorophyllides, and pheophytins in vari-
ous solvents. (Argonne Natl. Lab., Argonne, Ill.). J. Am. Chem. Soc.
85 (23), 3801-9 (1963). The infrared spectra of chlorophylls a and b
in CCl_4, $CHCl_3$, and benzene (nonpolar solvents) in the 1600-1750-cm^{-1}
region are best interpreted on the basis of intermol. aggregation in-
volving coordination of ketone and aldehyde carbonyl O atoms of 1 mol.
with the central Mg atom of another. In basic or polar solvents, the
coordination unsatn. of the Mg is satisfied by the solvent, and the
chlorophylls exist predominantly in monomeric form. Direct mol. wt.
detns. confirm the relation between the extent of mol. aggregation
and the observed infrared spectra.

Ke, Bacon

12
CA 61-16444e (1964)

Light-induced rapid absorption changes during photosynthesis. IV.
Reactions in aged chloroplasts in the presence of ascorbate and redox
dyes. (Charles F. Kettering Res. Lab., Yellow Springs, Ohio). Bio-
chim. Biophys. Acta 88 (2), 289-96 (1964)(Eng); cf. CA 61, 11064a.
Transient absorption changes at 430 mμ are induced in aged chloroplasts
by red light flashes. The absorption change occurs in 10^{-4} sec. or
less and has a half-life of approx. 10-2 sec. The enhancement of the
reaction by ascorbate and the abolishment by ferricyanide suggest that
an oxidn. reaction is responsible for the absorption change. In the
presence of 3-(3, 4-dichlorophenyl)-1, 1-dimethylurea, the absorption

change is not observed, but the signal can be restored completely by adding ascorbate. Available evidence ,from the decay kinetics of the 430-mμ transient absorption changes in the presence of ascorbate suggests that dichloroindophenol at all concns. reacts with cytochrome while phenazine methosulfate at low concns. reacts with cytochrome and at concns. > 3 x 10^{-5} M with the pigment complex P700 only. This is in accord with the difference spectra observed in the blue region (where also cytochrome changes are observed) and also with the concomitant and similarly decaying absorption changes at 430 and 703 mμ. Light-intensity dependency of the complex reaction in aged chloroplasts contg. ascorbate and a trace amt. of phenazine methosulfate showed that at low intensity only the oxidn. of the chlorophyll complex takes place. The coupling reaction between the pigment complex and cytochrome takes place only at higher light intensities.

Ke, Bacon   18, 17, 12
                                                             CA 64-2305d (1966)

Optical rotatory dispersion of a chloroplast preparation. (Kettering Res. Lab., Yellow Springs, Ohio). Nature 208 (5010), 573-4 (1965) (Eng). Observations are given on spinach leaf chloroplasts in soln., as well as in the natural environment, with regard to the relation between optical rotatory dispersion (ORD) and the binding of pigments in the photosynthetic process. Cotton effects corresponding to the major absorption bands in the red and blue regions indicated optical activity in the electronic transitions corresponding to the absorption bands. Paths of possible interaction of chlorophylls, carotenoids, and lipoproteins, and between pigment mols. and the attached macromols. are suggested.

Ke, Bacon   18
                                                             CA 64-5351a (1966)

Optical rotatory dispersion of chloroplast-lamellae fragments.
(Charles F. Kettering Res. Lab., Yellow Springs, Ohio). Arch. Biochem. Biophys. 112 (3), 554-61 (1965)(Eng). The optical rotatory dispersion (ORD) of the chloroplast-lamellae fragments shows Cotton effects corresponding to all the pigment-absorption peaks in the visible region and a neg. trough at 235 mμ. The ORD spectrum in the visible region shows considerably more complexity and intensity than that of the isolated chlorophylls or xanthophylls in an org. solvent. The enhancement of the intrinsic Cotton effects of the pigments in the lipoprotein suggests a strong interaction between the pigment mols. themselves and (or) between the pigment mols. and the attached lipoprotein macromols. The major contribution to the 235 mμ trough was attributed to protein conformation. Under this assumption, the

protein in the chloroplast lamellae was estd. to contain approx. 17% helix. Heating the chloroplast lamellae reduced the magnitude of the 235 mµ trough and shifted the characteristic ORD spectrum of the native lamellae to one resembling that of the free pigments. Urea treatment of the lamellae protein reduced the 235 mµ trough but did not affect the visible-region Cotton effects. Heating the lamellae possibly caused a disruption of the organizational relation between the pigment and the lipoprotein as well as the helical conformation.

Ke, Bacon and Miller, Robert M.   18, 17
                                               CA 61-14948h (1964)

Optical rotatory dispersion of chlorophyll a. (C.F. Kettering Res. Lab., Yellow Springs, Ohio). Naturwissenschaften 51 (18), 436 (1964) (in English). Results on the optical rotatory dispersion (ORD) of chlorophyll a (I) and chlorophyll b (II) from 350 to 700 mµ are reported. For I, typical Cotton effect curves indicated that the electronic transitions corresponding to the 2 major absorption bands were optically active. As measurements are made toward shorter wavelength in the red absorption band, the optical rotation decreased as the absorption max. was approached, reached a trough, and then rapidly increased until it reached a corresponding peak, and then gradually decreased again. The pattern was reversed in the blue absorption band. Expts. on II produced a similar ORD curve with the Cotton effects shifted in wavelength to correspond to positions of the absorption max.

Kholmogorov, V. E., Sidorov, A. N.   16, 14, 17
and Terenin, A. N.   CA 58-9363c (1963)

Light-induced electron spin resonance signals in chlorophyll in the crystalline state and its infrared spectrum. Dokl. Akad. Nauk SSSR 147, 954-7 (1962). The dark- and light-induced electron spin resonance spectra of cryst. chlorophyll are shown and correlated with the infrared spectrum. Cryst. pigment has a complex infrared spectrum in the 3400 cm^{-1} region, which indicates a special state of bound H_2O, which differs from that in the amorphous pigment. Specifically, a strong enolic shift is suggested for the cryst. form. Removal of bound H_2O results in a shift toward the keto form. It is suggested that the 3200 cm^{-1} band is caused by HO vibration of assocd. H_2O, and a narrow band at 3603 cm^{-1} is caused by unassocd. HO bond. Induction of the signal in cryst. chlorophyll is best accomplished by light with a 720 mµ wavelength. It appears to involve the transfer of an exciton, prior to liberation of current-carrying entities.

Kholmogorov, V. E. and Shablya, A. V.   4, 16, 1
CA 61-12824e (1964)

Investigation of the products of dark reduction of phthalocyanines by
metallic sodium using the electron paramagnetic resonance (E.P.R.)
method. Optika i Spektroskopiya 17 (2), 298-9 (1964). E.P.R. and
light absorption spectra of tetrahydrofuran solns. of Mg phthalocyanine
(MgPhc) were studied simultaneously. Dark redn. of MgPhc by metallic
Na (prepd. by thermal decompn. of its azide) leads to at least 2 prod-
ucts; only 1 of them exhibits an E.P.R. spectrum (g = 2.003, $\Delta H = 7$ oe.).
The corresponding neg. ion-radical with delocalized unpaired electron
is characterized by absorption max. at 420, 640, 950, and, probably,
570 mμ. Creation of the redn. products inactive in E.P.R. is explained
by consecutive reactions of the primary ion-radicals. The spectra of
the redn. products of phthalocyanine (no metal) are similar to those
described, the radical having also the absorption max. at 570 mμ.

King, Gerald W.   1

Spectroscopy and Molecular Structure. New York: Holt, Rinehart, and
Winston. 1964. 482 pp.

Klingmueller, V.   13, 4
CA 61-11140g (1964)

Chemistry and metabolism of porphyrins. Modern aspects. Arch. Klin.
Exptl. Dermatol. 219, 7 (13-18) (1964). A review. Protoporphyrinemic
light urticaria. I. Heilmeyer. Ibid. 717-18. Descriptions are given
of several forms of erythropoietic porphyria involving proto- and
light sensitivity.

Kravtsov, L. A. and Ivanov, N. P.   10, 15, 17
CA 52-11567c (1958)

Calculation of the influence of reabsorption in luminescence spectra
of pheophytin and chlorophyll. (Inst. Phys. and Math. Acad. Sci.
Beloruss. SSSR, Minsk). Inzhener.-Fiz. Zhur., Akad. Nauk Beloruss.
SSR 1958, No. 2, 45-52. The influences of the reabsorption are con-
sidered for the spectra of luminescent mols., where there is a strong
overlapping of the bands of the absorption and of the luminescence.
Chlorophyll and pheophytin are especially considered. Under various
conditions of excitation it is possible to calc. the reabsorption and
to obtain the true shape of the luminescence bands from the values as
measured.

Kobayashi, Hiroshi

The electronic structure and electronic spectra of porphyrins. I.
A naive molecular-orbital treatment of porphine. (Inst. Technol.
Tokyo). Nippon Kagaku Zasshi 81, 519-24 (1960). A naive M.-O. calcn.
was carried out on prototype porphine, the electronegativity parameter
of N being varied from 0.0 to 1.5. The orbital energies, transition
energies, electron ds., electron bond orders, free valences, and
frontier electron ds. were evaluated as the functions of the electro-
negativity parameter. It is predicted that both electrophilic and
radical reagents attack a porphine mol. at its N atoms or methine
bridges, whereas nucleophilic reagents do only at the methine bridges.
Various bands in the electronic spectrum could be interpreted as
arising from transitions to electronic configurations, in which a
single electron is excited.

Kobayashi, Hiroshi

The electronic spectra of porphine. (Tokyo Inst. Technol.). J. Chem.
Phys. 30, 1362-3 (1959). The excitation of prototype porphine was
studied through the semiempirical self-consistent field mol. orbital
theory. The energies of the lowest excited configurations and the
values of their interconfigurational matrix elements were summarized.

Kobozev, N. I., Nekrasov, L. I.
and Podgornyi, I. M.

Determination of magnetic susceptibility of adsorbed chlorophyll.
(State Univ., Moscow). Problemy Fotosinteza, Doklady 2-oi [Vtoroi]
Konf., Moscow 1957, 131-5 (Pub. 1959). The adsorption isotherm of
chlorophyll on alumina gel has an inflection corresponding to the
filling-up of the lst unimol. layer and the subsequent formation of a
2nd layer. While cryst. chlorophyll is diamagnetic, the adsorbed pig-
ment is paramagnetic, regardless of the degree of surface filling.
The magnetic susceptibility curve also has a sharp break at the point
of transition of uni- to bimol. layer state. The magnetic suscepti-
bility rises rapidly with decreasing degree of surface filling, and at
low filling values it reaches very large paramagnetic levels. The
results are shown graphically.

Kobyshev, G. I., Lyalin, G. N. and   15, 17
Terenin, A. N.   CA 65-6534f (1966)

Luminescence of chlorophyll excited by a ruby laser. (A. A. Zhdanov
State Univ., Leningrad). Dokl. Akad. Nauk SSSR 168 (1), 68-71 (1966)
(Russ). A new luminescence band, 430-510 mμ, peaking at 480, was ob-
served in 5 x 10^{-3}M solns. of chlorophyll a and methylchlorophyllide in
EtOH and of chlorophyllin in MeOH upon ruby laser excitation. The life-
time of the emission was 0.1 msec. at 25°, and no emission was seen at
at -196°. The band is red-shifted with respect to the 430-mμ Soret
band and is believed to be emission from S_2^*, the 2nd excited singlet.
The absence of such an emission in solns. of phthalocyanine (I), with or
without Mg, rules out a mechanism of radiative recombination of ions or
ion radicals arising from interaction with the solvent. A diffusion-
controlled triplet-triplet annihilation leading to S_2^* seems more likely,
although the absence of O quenching cannot be explained. The triplet
level in I is known to be less than half that of S_2^*.

Kok, Bessel and Hock, George   12
                                                   CA 55-13485f (1961)

Spectral changes in photosynthesis. (Research Inst. for Advanced
Studies, Baltimore, Md.). Ibid. 397-416. IN: Symposium on Light and
Life, Johns Hopkins University, 1960, Light and Life: proceedings.
Edited by William D. McElroy and Bentley Glass. (Johns Hopkins Uni-
versity. McCollum-Pratt Institute. Contribution No. 302).

Koziol, J.   1, 8, 15, 13
                                                   CA 63-1354d (1965)

Absorption spectra of riboflavine, lumiflavine, and lumichrome in
organic solvents. (Central Res. Inst. Food Ind., Prague). Experientia
21 (4), 189-90 (1965)(Eng). During extensive investigations made to
det. the effect of org. solvents on fluorescence emission and absorp-
tion spectra, it was found that riboflavine (I) in abs. EtOH, acetone,
and 1, 4-dioxane mixts. with water and lumiflavine (II) in pure sol-
vents photodecompd. more rapidly when illuminated with visible light
than in aq. solns. Lumichrome (III) was a product of photodecompn.
The absorption spectra of the 3 compds. in these mentioned solvents
showed that the photolability increased as a result of a decrease of
dissocn. and assocn. degree of I, II, and III with solvent mols. Com-
pared to the spectra of these compds. in aq. solns., significant
shifts of near-uv max. were noted as the result of solvent polarity,
and for I and II, a decrease of absorbency in this max. occurred as
the result of solvent assocn. III also showed a new max. at 248 mμ
and increased absorbency at the longest wavelength max.

Koziol, Jacek

Studies on flavines in organic solvents. I. Spectral characteristics
of riboflavine, riboflavine tetrabutyrate, and lumichrome. (Central
Res. Inst. Food Ind., Prague). Photochem. Photobiol. 5 (1), 41-54
(1966)(Eng). The absorption and fluorescence spectra of riboflavine
(I), riboflavine tetrabutyrate (II), and lumichrome (III) were detd.
in H_2O, EtOH, Me_2CO, dioxane, pyridine, AcOH, and cyclohexane-dioxane
mixts. The changes observed in the absorption spectra were discussed
in terms of H-bonding effects and intramol. charge transfer complexes.
Changes in the fluorescence spectra were less obvious; in the case of
II, mirror symmetry to the shape of the longest wavelength max. was
seen in low-polar solvents. Fluorescence quantum yields were greater
in solvents of lower polarity and also greater for II than for I.
For III there was a shift of the fluorescence max. towards longer wave-
lengths with increasing polarity of the solvent.

Koziol, Jacek

Studies on flavines in organic solvents. II. Photodecomposition of
riboflavine in the presence of oxygen. (Central Res. Inst. Food Ind.,
Prague). Photochem. Photobiol. 5 (1), 55-62 (1966)(Eng); cf. preced-
ing abstr. Photodegradation of riboflavine (I) by 436 mµ monochro-
matic light and of lumichrome (II) by white non-filtered light was
studied in H_2O, EtOH, Me_2CO, dioxane, pyridine and AcOH in the presence
of atm. O. I and II were stabilized by H-bonding with solvent mols.
and were thus most light-stable in H_2O solns. The overall scheme of
photolysis of I in org. solvents was the same as in aq. solns.; II was
the main product of photolysis of I in org. solvents.

Koziol, Jacek and Knobloch, Eduard

The solvent effect on the fluorescence and light absorption of ribo-
flavine and lumiflavine. (Central Res. Inst. Food. Ind., Prague).
Biochim. Biophys. Acta 102 (1), 289-300 (1965)(Eng). Changes in
fluorescence intensity of riboflavine and lumiflavine with the nature
of the solvent were studied. A series of mixts. of EtOH, acetone,
and dioxane with water was used as solvents. Changes in absorption
and fluorescence spectra expressed as transition energies, apparent
absorption coeffs. and quantum yields of fluorescence were correlated
with each other, with dielec. consts., and with the Z-values expres-
sing solvent polarity of the solvent mixts. used. Rough linearity was
observed for all parameters, except dielec. consts., for flavine solns.

contg. $\leqq$ 90% of org. solvent. In riboflavine solns. contg. higher
concns. of org. solvents deviations from linearity were observed.
The possibility is discussed, that in such higher concns. of org.
solvents relative measurements accepted do not adequately reflect
changes in flavine mols. In solvent mixts. of lowest polarity ribo-
flavine and, to a greater extent, lumiflavine were photodecompd. much
faster than in aq. solns. It is suggested that the decrease of the
stability of flavine mols. is caused by lowering of the degree of
assocn. with water mols., and by a secondary polarity effect on the
electron system of light-excited flavine mols.

Krasnovskii, A. A., Nesterovskaya, E. A.   1, 17
and Gol'denberg, A. B.   CA 50-17016d (1956)

Spectroscopic studies of the composition of chlorophyll in red algae
phylophora. (A. N. Bakh Biochem. Inst. Acad. Sci., U.S.S.R., Moscow)
Biofizika 1, 328-33 (1956). Kirillov's (Monography, Moscow (1954))
app. was used for spectrophotometric measurements. The studies were
carried out with leaves of the algae and the solns. of the pigments
in 80% acetone and MeOH at room temp., 40, 60, and 80°. The algae
were collected from the depth of 20-5 m. of sea, from May to January.
The 3 max. of absorption were found at 670, 675-8, and 685-90 mμ. The
relative intensity of above absorption varied with the seasons. In
the spring, together with the greater max. at 675-8 mμ, is present also
max. at 690 mμ. In the fall both max. were moved to 675-85 mμ. The
heating (5-15 min.) of algae to 60 and 80° produced the moving of the
max. to 671-2 mμ. The solns. of chlorophyll (contg. both green and
yellow pigments) in 80% acetone and MeOH from these algae gave only
max. of absorption at 664 mμ, corresponding to chlorophyll a. Judged
by the previous studies the presence of above 3 max. of absorption
depends on variations in the degree of polymerization of chlorophyll
in these algae.

Krasnovskii, A. A.   13, 17, 1, 12
                                                  CA 64-2305e (1966)

Photochemistry and spectroscopy of chlorophyll, bacteriochlorophyll,
and bacterioviridin in model systems and photosynthesizing organisms.
(Acad. Sci. U.S.S.R., Moscow). Photochem. Photobiol. 4 (4), 641-55
(1965)(Eng). A review with 67 references in which electron and energy
transfer in photoprocesses is discussed.

Krasnovskii, A. and Pakshina, E. V.   13, 17
                                                       CA 58-12815c (1963)

A comparative study of formation of pheophytins from chlorophyll and
its analogs in the dark and in light. (A. N. Bakh Biochem. Inst.,
Moscow). Dokl. Akad. Nauk SSSR 148, 935-8 (1963). Photopheophytini-
zation takes place through an intermediate formation of labile photo-
reduced products and involves the excited mols. of chlorophyll or its
analogs which react with $(CO_2H)_2$ or solvent mols., which act as proton
donors. Pheophytin is the end product of a stable type, although the
reaction sequence is properly reversible. The results were deduced
from examn. of absorption spectra of systems of chlorophylls a and b,
bacterioviridin, protochlorophyll, and bacteriochlorophyll in photo-
chem. reactions in aq. Me_2CO or aq. pyridine in the presence of either
$(CO_2H)_2$ or HCl. Naphthacene inhibited the reaction in aq. pyridine in
the presence of HCl. A very rapid reaction in pyridine was observed
only in the case of bacterioviridin; the rate of Mg replacement in this
pigment was the same in the dark as in light. In other pigments, the
reaction was definitely stimulated by light.

Krasnovskii, A. A., Bystrova, M. I.   1, 17, 13
and Pakshina, E. V.   CA 64-20068e (1966)

Effect of magnesium atom in the pigment molecule on the spectral
properties of aggregated forms of chlorophyll analogs. (A. N. Bakh
Biochem. Inst., Moscow). Dokl. Akad. Nauk SSSR 167 (3), 691-4 (1966)
(Russ). Spectra were reported for aggregated forms of bacterioviridin
and its Mg-free analog in solid films and in bacterial cells, in com-
parison with aggregated forms of other pigments (chlorophylls a and b,
pheophytins a and b). The aggregated forms of pigments with bands in
the 740-750 mμ region are characterized by intermol. interaction of the
central Mg atom. The 690-mμ form of bacterioviridin appears to have a
different form of intermol. bonding, the nature of which is not known.

Krasnovskii, A. A. and Drozdova, N. N.   15, 17
                                                       CA 64-11474b (1966)

A comparative study of the quenching of the fluorescence of chlorophyll
and its analogs; action of carotene on the quenching effect. (A. N.
Bakh Biochem. Inst., Moscow). Dokl. Akad. Nauk SSSR 166 (1), 223-6
(1966)(Russ). Quenching of the fluorescence of chlorophyll, pheophy-
tin, protochlorophyll, bacteriochlorophyll, and bacterioviridin was
examd. in the presence of O and p-benzoquinone. The quenching effect
did not correspond to the degree or the rate of photochem. reaction
between these reactants. Pheophytin fluorescence was strongly quenched

by O, although this pigment is very difficult to oxidize by O, and this quenching was greater than that observed with the easily oxidized bacteriochlorophyll. A correlation must thus be sought between quenching and the primary, rapidly reversible photochem. processes. Carotene partially inhibited the quenching effect of O and p-benzoquinone.

Krasnovskii, A. A., Erokhin, Yu. E. and Hung, Yu-Chiung

15, 17, 12
CA 57-3857d (1962)

Fluorescence of aggregated forms of bacteriochlorophyll, bacterio-viridin, and chlorophyll in connection with the state of the pigments in photosynthesizing organisms. (A. N. Bakh Biochem. Inst., Moscow). Dokl. Akad. Nauk SSSR 143, 456-9 (1962); cf. CA 55, 11558a. Fluorescence spectra are reproduced for specimens of: bacteriochlorophyll in a film and in Rhodopseudomonas palustris culture at various temps. for bacterioviridin in solid film and in Chlorobium culture, and for a chlorophyll film and a typical green leaf of the bean plant for reference. The quasicrystalline densely packed bacteriochlorophyll showed weak luminescence at 850-90 mμ at 20°, while at -196° the luminescence was much stronger with a shift to 910-20 mμ. Adsorbate on sucrose fluoresced weakly at 810 and 880 mμ, at room temp., while at -196° high intensities appeared at 820 and 915 mμ, resp. Bacterioviridin had weak luminescence in film form at 20° (780-90 mμ) but intense effect at -196° (805-10 mμ); its colloidal solns. or sucrose adsorbates fluoresce at 780-90 mμ at room temp. or 780-800 mμ at -196°. The results indicate that a definite type of packing of aggregated pigments is responsible for a specific type of luminescence. In case of chlorophyll the fluorescence max. at 810-5 mμ seen in normal leaves also exists in films of the pigment but not in dil. solns. The structural peculiarities of the aggregated pigments may be related to the general problem of existence of photosynthetic activity in plants.

Kravtsov, L. A.

1, 17
CA 54-22000g (1960)

Optical properties of chlorophyll and pheophytin at low temperatures. Izvest. Akad. Nauk S.S.S.R., Ser. Fiz. 24, 610-12 (1960). The absorption and luminescence spectra of solns. of chlorophyll a and pheophytin a in iso-BuOH and petr. ether were measured (frozen) at 20 to -100°. All measurements were made in the red band. At lower temp. the bands get narrower and the absorption and luminescence peaks move towards one another. The relative yield decreases with decreasing temp. in chlorophyll a and in pheophytin a in petr. ether soln.; this indicates an aggregation to some nonluminescing compd.

Kreutzberger, Alfred and Kalter, Paul A.   14, 7

Infrared studies on pyrroles. The structure of 2, 5-diphenylpyrrole-3-diazonium chloride. (Ford Motor Co., Dearborn, Mich.). J. Phys. Chem. 65, 624-8 (1961). The infrared spectra of pyrrole, 2, 5-dimethylpyrrole, 2, 5-diphenylpyrrole, 1-methylpyrrole, and 1-phenylpyrrole were measured at 4000-670 cm^{-1}, and the correlations of the absorption bands to the vibrational elements were detd. On the basis of these spectra 3-diazo-2, 5-diphenylpyrrole (I) was shown to be a resonance hybrid. The structure of I.HCl was shown to be 2, 5-diphenylpyrrole-3-diazonium chloride.

Kudo, Shuji and Iwamoto, Hisaichi   2, 16

γ-Ray irradiation effects on porphyrin compounds. A geochemical study related to the origin of petroleum. (Sekiyu Shigen Kaihatsu Co., Tokyo). Sekiyu Gijutsu Kyokai-shi 29 (6), 262-7 (1964)(Japan). Cu chlorophyllin Na salt (I), 10-100 mg., in 20 ml. glass ampuls, were irradiated by ^{60}Co γ-rays of 10,000 c. The effects of H_2O, aq. NaCl, and rock powder suspended in aq. NaCl were examd. by adding them into the ampuls. The changes of the I concn. were measured by the absorbance at 650 mμ and the reaction ratios were calcd. The desalting of I by γ-ray irradiation is a 1st-order reaction of the radiation dose. In $d(1-x)/dr = k-(1-x)$, where x is the reaction ratio, and r is the amt. of radiation, the reaction coeff., k, was calcd. to be 0.52×10^{-8}. The values of k were larger, when I was in H_2O or aq. NaCl, esp., when the rock powders were suspended in the soln. The gases formed were analyzed by gas chromatography on squalene, SiO_2 gel, and mol. sieve columns, and H, O, N, CO_2, CH_4, C_2H_4, C_2H_6, and C_3H_8 were found. The results were discussed from the geochem. point of view.

Kuhn, Hans   10, 13

A quantum-mechanical theory of light absorption of organic dyes and similar compounds. (Univ. Basel, Switz.). J. Chem. Phys. 17, 1198-1212 (1949). See CA 44, 433e.

7129-Final

Kuhn, Werner   1
                                                    CA 43-1654b (1949)

The absorption spectrum of polyenes. Helv. Chim. Acta 31, 1780-99
(1948) (in German). Based on the theory of equiv. resonators for the
atoms or atom groups, a simple model is developed for polyenes with
n conjugated double bonds, whose spectrum can be calcd. from the
frequency of the isolated ethylene absorption band as well as a sin-
gle characteristic const. for the coupling. Calcn. of the longest
wave absorption band of a system, from $v_x = 1.91 \times 10^{15}(1 - 0.992 \cos$
$(\pi x/n+1))^{1/2}$ where x = 1 agrees with the exptl. results for the
carotenoids. The intensity increases proportionally with n. For
shorter-wave vibrations x = s and the intensity is very much smaller.
The numerical value of the coupling coeff. is so large that an in-
crease of 10% would lead to a free displacement of the electrons in the
chain, and H. Kuhn's electron gas model (cf. preceding abstract).

Lang, Laszlo, ed   1
                                                    CA 53-21207a (1959)

Absorptionsspektren im ultravioletten und im sichtbaren Bereich.
Budapest: Akadémiai Kiadó. 1959. 499 pp.

Latimer, Paul and Rabinowitch, Eugene I.   13
                                                    CA 52-10303b (1958)

Selective scattering of light by pigment-containing plant cells.
(Univ. of Illinois, Urbana). 100-6; cf. CA 50, 6595b. Discussion
and 7 references.

Lemberg, R. D., Morrell, D. B., Newton, N.   1, 9, 5
and O'Hagan, J. E.

Haem a Compounds as Models for Cytochromes of Group a. I. Absorption
Spectra of Haem a Compounds with Proteins and other Nitrogenous
Ligands. Proc. Roy. Soc. (London), Ser. B, 155 (1961) p. 339.

Lemberg, R. and Mansley, G. E.   5, 1
                                                    CA 62-10729h (1965)

Cytochrome c oxidase and its derivatives. IV. The ferric-ferrous
isosbestic points of cytochrome a and a_3. (Inst. Med. Res. Roy. North
Shore Hosp., Sydney). Biochim. Biophys. Acta 96 (2), 187-94 (1965)
(Eng); cf. CA 60, 12286h. Ferric cytochrome a is reduced much faster

by dithionite than is ferric cytochrome a_3. This has made it possible to differentiate between the 2 cytochromes by the ferric-ferrous isosbestic points of their absorption curves in the region of the γ (Soret) band. The 2 isosbestic points of cytochrome a were found at about 436 and 461 mμ, those of cytochrome a_3 at 428 and 466 mμ, while their mixt. (cytochrome oxidase) has isosbestic points at 432 and 463 mμ. The findings are in harmony with the assumption that the molar ratio of the 2 cytochromes is 1:1 and confirm that cytochrome oxidase contains 2 cytochromes, a and a_3.

Lemberg, R.   2, 13
                                                    CA 49-2295f (1955)

Porphyrins in nature. (Roy. North Shore Hosp., St. Leonards, Sydney). Ibid. 229-349. The pteridines. Adrien Albert (Australian Natl. Univ., Canberra). Ibid. 350-403. Reviews with many references, cf. CA 47, 3370i.

Lemberg, R. and Falk, J. E.   9, 2
                                                    CA 46-5578a (1952)

Comparison of hem a, the dichroic hem of heart muscle, and of porphyrin a with compounds of known structure. (Roy. North Shore Hosp., Sydney, Australia). Biochem. J. 49, 674-83 (1951). Three types (etio, rhodo, and oxorhodo) of absorption spectra of porphyrins in the visual region (neutral solvents) have been described.

Lemberg, R. and Stewart, M.   13, 2

Porphyrins with Formyl Groups VI: Purification and Properties of Porphyrin a. Australian Journal of Experimental Biology and Medical Science, Vol. 33 (1955), p. 451-481.

Lemberg, R., Falk, J. E., Rawlinson, W. A.   9, 2, 13
Hale, J. H. and Rimington, C.

Comparison of Haemin a with Known Formyl-Containing Porphyrins. 1st International Congress of Biochemistry, Cambridge (1949), p. 351-2.

Lemberg, R. and Parker, J.   2, 11

Prophyrins with Formyl Groups II. Preparation of Chlorocruoroporphyrin and Diformyl-Deuteroporphyrin. Australian Journal of Experimental Biology and Medical Science, Vol. 30 (1952), p. 163-175.

Lemberg, R., Clezy, P. and Barrett, J.   2, 11

The Structure of Porphyrin a, Cryptoporphyrin a and Chlorin a_2.
Haematin Enzymes, Vol. 19 Part 1 (1959) p. 344-357, Pergamon Press.

Lester, G. R.   16
                                                        CA 65-11512g (1966)

Electronic aspects of the structure and mass spectra of large ring
systems. (Imp. Chem. Inds. Ltd., Manchester, Engl.). Mass Spectrome-
try, NATO Advan. Study Inst., Glasgow 1964, 153-81 (Pub. 1965)(Eng).
Electron impact processes and transition probabilities, stability
criteria for ring systems and their ionized forms, mechanisms for
multiple ionization, metastable transitions, electronic states of
multiply charged ions, and configuration interaction effects in multi-
ple excitation processes in phthalocyanines are reviewed. 20
references.

Levi, Georges   14, 7
                                                        CA 66-6781a (1966)

Absolute intensity of the infrared absorption of pyrrole in the vapor
phase and in solution. (Fac. Sci., Paris). Compt. Rend., Ser. A, B
263B (7), 493-5 (1966)(Fr). The abs. intensity of the ν(NH) band of
pyrrole in the vapor phase and in soln. in a series of polar and non-
polar solvents was measured. The linear relation between the abs.
intensity of the ν(NH) and the dielec. const. and n of the solvent
confirms the theory of Buckingham (Proc. Roy. Soc. (London) A248,
169 (1958).

Linnel, Robert H.   14, 7
                                                        CA 62-3532c (1965)

Hot band in the infrared spectrum of pyrrole. (Natl. Sci. Found.,
Washington, D.C.). J. Chem. Phys. 41 (10), 3274-6 (1964). Dil. CCl_4
solns. ($\sim$ 0.001M) of pyrrole show an ir absorption at 3480 cm^{-1} on
the side of the 3498-cm^{-1} fundamental N-H stretch. The 3480-cm^{-1}
absorption increases as the temp. increases and the 3498-cm^{-1} decreases
with increasing temp. A plot of ln (a_{3480}/A_{3498}) vs 1/T yields a
straight line; from the slope, $\bar{\nu} \cong 400$ cm^{-1}, which is identified with
the N-H out-of-plane deformation (503 cm^{-1} in non-H-bonded pyrrole).

Linshitz, Henry   17, 13
                                         CA 55-5609h (1961)

Studies on the photochemistry of rhodopsin and chlorophyll. (Brandeis
Univ., Waltham, Mass.). Ibid. 182-95.

Linshitz, H. and Weissman, S. I.   16, 17

Search for Paramagnetic Resonance Absorption in Photoreduced
Chlorophyll.

Litvin, F. F. and Sineshchekov, V. A.   14, 17
                                          CA 64-14482c (1966)

The nature of the long wave form of chlorophyll in photosynthetic
organisms. Molekul. Biofiz., Akad. Nauk SSSR, Inst. Biol. Fiz., Sb.
Statei 1965, 191-203 (Russ). The spectra of the low temp. (-196°)
luminescence of Chlorella suspensions, bean leaves, and chlorophyll
films were measured after monochromatic excitation in the range 430-
750 mμ. Several discrete max. were obtained in the range 670-825 mμ.
They are considered to be due to aggregates of the chlorophyll mols.

Litvin, F. F. and I-T'an Ho   12
                                          CA 65-4268d (1966)

Spectra of action of photosynthesis and the Emerson effect in higher
plants. (State Univ., Moscow). Dokl. Akad. Nauk SSSR 167 (5),
1187-90 (1966)(Russ). The action spectrum of photosynthesis was
examd. in Elodea and had 4 max. at 650, 480-500, 430, and 650 mμ.
The "red" decline of quantum yield of photosynthesis was found in the
longer wavelength end of the spectrum (685 mμ) and reached 65-70%.
With pigment accumulation in etiolated leaves, the action spectrum
changed by developing a max. at 670 mμ and shoulders at 685 and 650
mμ. The Emerson effect was observed by making use of proper intensi-
ties of red (650 mμ) and far red (717 mμ) wavelengths of light; the
Emerson effect for Elodea was some 60%. With monochromatic illumina-
tion, the kinetics of O evolution showed a very decided effect on light
wavelength; with long wavelength light alone, the O production curve
does not have an induction period; that produced by light in the
vicinity of 650 mμ is similar to the curve produced by white light.
Repeated illumination with 650-mμ light led to smoothing of the curves
and shortening of the induction period. Light with 700 mμ or longer
wavelengths produced a neg. peak of O absorption. With both rapidly
alternating 650-mμ and 690-mμ wavelengths operating, the plants under-
went a severe redn. of O production.

Litvin, F. F., Gulyaev, B. A.   17, 3
and Sineshchekov, V. A.   CA 63-7253f (1965)

Aggregated forms of chlorophyll a, chlorophyll b and β-carotene.
(State Univ., Moscow). Dokl. Akad. Nauk SSSR 162 (5), 1184-7 (1965)
(Russ). Absorption spectra were reported for monolayers and films of
title pigments. β-carotene in monolayers gave a spectrum in which
the absorption was shifted toward longer wavelengths with predominance
of the 520-mμ max.; in stored films a new form of the pigment was
found; this absorbed in 536-40 mμ region. The spectral shift was
explained by a more densely packed and aggregated state. Chlorophyll-
carotene mixts. made into film gave an additive spectrum only with
relatively large excesses of carotene; at other levels the spectrum
had max. that were not produced by fresh monolayers of β-carotene.
With predominance of chlorophyll, the spectrum had a strong max. at
500-10 mμ. Energy transfer between carotene and chlorophyll was
studied by excitation of luminescence spectra in mixed films; transfer
efficiency of 40-50% was observed and a sensitization effect was found
in that carotene stimulated the luminescence of chlorophyll in a spec-
trum that had the same max. as produced by K_{500} form of carotene.
Illumination of such mixed films reduced the intensity of the max. at
500 mμ and 520 mμ. Aggregated forms of chlorophyll b were detected
in monolayers and films of this pigment and their spectra were shown.
The red shift of the spectrum of the long wavelength forms of these
pigments was explained by aggregation or polymerization of the chromo-
phores, many of which forms are observable in soln. and are evidently
not connected with the monolayer structure as such.

Litvin, F., Sineschekov, V. A,   14, 12, 17
and Krasnovskii, A. A.   CA 60-10974d (1964)

Long-wave forms of chlorophyll in photosynthesizing organisms and
aggregated structures. (State Univ., Moscow). Dokl. Akad. Nauk
SSSR 154 (2), 460-2 (1964). Chlorophyll films retaining small amts.
of org. solvents were studied spectrometrically at low temps. Gen-
erally, low temp. caused increased intensity to develop in the longer
wavelength maxima and caused relatively little change in luminescence
in the shorter wavelength part of the spectra. These changes were
similar to those observed in natural forms of chlorophyll in Chlorella
or green leaves in situ. Thus, the bands at 682-5, 693-6, 720, 730,
and 810-25 mμ are ascribed to naturally aggregated forms of chlorophyll.

Litvin, F. F. and Personov, R. I.   1, 15, 4, 2
                                                      CA 59-12296h (1963)

Fine structure of absorption and fluorescence spectra of phthalocyanine
and protoporphyrin.   (Lenin State Ped. Inst., Moscow).   Fiz. Probl.
Spektroskopii, Akad. Nauk SSSR, Materialy 13-go [Trinadtsatogo]
Soveshch., Leningrad, 1960,1, 229-30 (Pub. 1962).   Exptl. data are
given on absorption and fluorescence spectra of phthalocyanine (free
of metal), Mg phthalocyanine, and protoporphyrin at 77°K in n-octane
solns.   (Shpol'skii, CA 54, 23838g).

Livingston, Robert   13, 17
                                                      CA 52-10302g

Photochemistry of chlorophyll in vitro.   (Univ. of Minnesota,
Minneapolis).   Pages 3-16.   Discussion and 7 references.

Livingston, R. and McCartin, P. J.   17, 12
                                                      CA 59-1215b (1963)

Photoreduction of chlorophyll.   (Univ. of Minnesota, Minneapolis).
J. Am. Chem. Soc. 85, 1571-3 (1963).   The efficiency of quenching of
the triplet state of chlorophyll a by ascorbic acid in pyridine in-
creases with the water content of the solvent.   The bimol. quenching
const. is approx. $10^4 M^{-1} sec^{-1}$ for dry pyridine, but increases to
about 1.5 x 10^5 M^{-1} sec^{-1} for pyridine contg. 25% water.   The quench-
ing of the triplet is accompanied by the formation of a labile inter-
mediate, with absorption spectrum which has a max. near 480 mμ.   Under
these exptl. conditions, the decay of this intermediate was 1st order,
with a half-life of $\sim$ 10 msec.   The product of this decay is, in part,
Krasnovsky's pink pigment.

Livingston, Robert

17, 12
CA 55-5609h (1961)

Photochemistry of chlorophyll related to the primary act of photosynthesis. (Univ. of Minnesota, Minneapolis). Ibid. 196-217.

Livingston, Robert and Fujimori, Eiji

1, 17
CA 53-10998e (1959)

Some properties of the ground triplet state of chlorophyll and related compounds. (Univ. of Minnesota, Minneapolis). J. Am. Chem. Soc. 80, 5610-13 (1958). A flash photolytic-flash photographic technique was used to measure the absorption spectra of the lowest triplet states of chlorophyll-a and -b, pheophytin-a and -b, Zn chlorophyll-a, Zn protoporphyrin, protoporphyrin, mesoporphyrin, tetraphenlychlorin, and Mg phtalocyanine in air-free C_6H_6 (wet and dry), MeOH, or pyridine solns. The principal absorption max. of the ground state are replaced in the triplet state by a broad absorption having a max. on the long-wave length side of the Soret band, which decreases gradually toward the red. No transients were detected for Cu^{++}- and Fe^{++}-protoporphyrin in MeOh, Fe^{+++}-protoporphyrin in either MeOH or pyridine, Cu^{++}-chlorophyll-a in benzene, β-carotene in C_6H_6, p-benzoquinone in C_6H_6 or p-nitroaniline in MeOH.

Livingston, Robert

17, 11, 12
CA 54-25082i (1960)

The photochemistry of chlorophyll in vitro. (Univ. of Minnesota, Minneapolis). Ibid. 138-144. Review of spectral transitions in chlorophyll. 18 references. The evolution of organic photochemistry on earth. Hans Gaffron (Univ. of Chicago). Ibid. 145-156. - A review with 9 references. The use of solar energy in the preparation of organic compounds, with special reference to the photochemistry of aldehydes and ketones.

Longuet-Higgins, H. C., Rector, C. W. and Platt, J. R.

10, 2
CA 45-2776f (1951)

Molecular orbital calculations on porphine and tetrahydroporphine. (Univ. of Chicago). J. Chem. Phys. 18, 1174-81 (1950); cf. preceding abstr., also Simpson, C. A. 44, 5164e. The first 3 electronic transitions of porphine and the first 5 electronic transitions of tetrahydroporphine are predicted as simple one-electron linear combination of at. orbitals mol. orbital transitions (with overlap included). The electron d. and bond orders in the ground states are also computed. The observed levels are tentatively assigned to the predicted levels with the help of comparisons with spectra of other aza-amine derivs.

of conjugated hydrocarbons. Probable degeneracies and polarizations
are detd. The blue shift and loss of intensity of the first electronic
transition, in going from tetrahydroporphine to the larger conjugated
system of porphine, is typical of the change from a "long-field" to
a "round-field" mol. and is shown to occur in several other "long-field"
systems when addnl. conjugated atoms are added at the side of the system.

Lundegardh, H.   1, 15, 12, 3
                                                  CA 65-20512g (1966)

Action spectra and the role of carotenoids in photosynthesis. (Res.
Lab., Penningby, Swed.). Physiol. Plantarum 19 (31), 754-69 (1966)
(Eng); cf. CA 65, 4270e. The action spectrum of photosynthetic O pro-
duction was detd. with suspensions of chloroplasts and whole leaves.
Due to a dominating influence of light scattering, the action spectrum
showed a more uniform absorption of the incident light than was expected
from the absorption spectrum in direct light. The comparatively strong
photosynthesis in green light may be further aided by the light reaction
between cytochrome f and chlorophyll in which the cytochromes act as
pigments. The whole region from 400 to 900 mμ is photosynthetically
active, with a tendency to a linear relation between the intensity of inci-
dent radiation and photosynthetic O production. The results suggest the
participation of carotenoids in the primary energy conversion of pho-
tons to activated electrons and of at least 2 light reactions in the
photosynthetic cycle. The reducing power of illuminated β-carotene
was demonstrated in vitro in its effect on ferredoxin. 18 references.

Lundegardh, H.   5, 11
                                                  CA 57-10226e (1962)

Response of chloroplast cytochromes to oxygen. Physiol. Plantarum 15,
399-408 (1962); cf. preceding abstr. Two instruments were used to-
gether. A double spectrophotometer recorded separately a sample and
a reference at precise wavelength intervals of 2 mμ; and a scanner
rapidly recorded a portion of the spectrum at wavelengths correspond-
ing to band peaks and points of reference. Time intervals of 0.2-40
sec. were used. With short flashes (0.25-2 sec.) green chloroplasts,
with and without O, showed differences at 558 and 564 mμ, corresponding
to cytochromes b_3 and b. At longer flashes a peak appeared at 554,
corresponding to cytochrome f. Expts. with the particulate fractions
(preceding abstr.) failed to give conclusive evidence as to what part
of the photosynthetic cycle which leads from cytochrome b_3 to activated
chlorophyll is accelerated in the presence of O.

Lundegardh, H.

Spectral changes in chloroplast pigments in relation to oxygen, light
and substrates. Physiol. Plantarum 16 (2), 442-53 (1963)(in English);
cf. CA 57, 10226c; following abstr. When spinach chloroplasts were
illuminated a no. of neg. bands appeared in the absorbance spectrum.
Bands at 554, 558, and 562-564 mμ (cytochromes) and 700 mμ were pre-
viously known, but bands at 500 and 640 were new. A no. of these
spectral differences also appeared in the dark when the atm. was changed
from N to O and were probably due to reversible oxidn. of pigments.
The 500 mμ band was attributed to carotenoids, and was strongly influ-
enced by redox changes in triphosphopyridine nucleotide. The 640 mμ
band was influenced by the steady state of adenosine di- to triphosphate,
and was probably involved in the oxidn. of the cytochromes. The spec-
trum of chlorophyll b, but not of a, was influenced by O. The results
are discussed in terms of 2 enzyme systems in photosynthesis.

Lyons, L. E.

First-order calculation of factor group splittings in the electronic
spectra of durene, ovalene, and phthalocyanine crystals. (Harvard
Univ.). J. Chem. Soc. 1958, 1347-51. First-order calcn. of the
values of integrals and splittings for durene, ovalene, and phthalo-
cyanine have been made from the mol. (soln.) spectra. These results
are applied to predict the crystal spectra of these compds.

Lyons, L. E., Walsh, J. R. and
White, J. W.

Phthalocyanine crystal spectra. (Univ. Sidney). J. Chem. Soc. 1960,
167-75. The theory of the crystal splitting of the intense absorption
bands in single metal-free crystals is employed to make quant. pre-
dictions of spectra. Exptl. polarized spectra are reported which differ
from the predicted quant. by the order of the bands, the energy sepa-
rating the bands, and the intensity of the bands. The 2 components
of lower energy appear in the predicted sequence, but the other 2 do
not. The sepns. of the various bands agree in magnitude, but the pre-
dicted spread, 13,000 cm.$^{-1}$, of the bands for the 15,000-cm.$^{-1}$ wave-no.
system is much greater than that observed, 1860 cm.$^{-1}$ Differences be-
tween predicted and observed intensities occur in both polarizations.
The theory is deficient insofar as it relies upon exptl. detd. inten-
sities, and bands which are not of the required negligible width. It
is concluded that, in spite of these inadequacies, observations are con-
sistent with the assumption of a pair of upper-energy states which are
similar to the lower-energy states in symmetry; this is in agreement
with the expectations based on M.O. theory.

Mangum, Charlotte P. and Dales, Phillips R.   11, 9
                                                CA 63-6059b (1965)

Products of heme synthesis in polychetes. (Univ. London). Comp.
Biochem. Physiol. 15 (2), 237-57 (1965 Eng). The porphyrins and
metalloporphyrins of different organ systems of 15 species of polychetes
were exd. by chromatography on Sephadex G-25 or G-75, or alumina columns
and identified by spectrophotometry or spectroscopy. The chem. charac-
teristics of the numerous porphyrins and derivs. are discussed in full
detail. The deduced pathway of heme biosynthesis in these worms differs
from that in vertebrates, in that prophyrin by-products accumulate in
nonsynthesizing tissues and then are converted to metalloporphyrins.

Marcus, Rudolph J. and Haugen, Gilbert R.   15, 17
                                                CA 62-16551g (1965)

Resonance fluorescence in chlorophyll a solutions. (Stanford Res. Inst.,
Menlo Park, Calif.). Photochem. Photobiol. 4 (2), 183-92 (1965)(Eng).
In aq. hexane solns. chlorophyll a (I) has 2 sets of fluorescence peaks,
2 fluorescence excitation peaks in the blue and 2 in the red. One
of these sets (excitation 2.34 μ^{-1} and 1.52 μ^{-1}, fluorescence 1.50 μ^{-1})
is the same as that of I in MeOH soln. and is assigned to an unaggregated
species, while the other (excitation 2.44 μ^{-1} and 1.475 μ^{-1}, fluorescence
1.48 μ^{-1}) is assigned to a species aggregated in the presence of H_2O.
The sharply increased overlap of absorption and fluorescence causes an
exptl. demonstrable resonance fluorescence in the aggregate.

Margoliash, E. and Lustgarten, J.   5
                                               CA 56-7670h (1962)

The chromatographic forms of cytochrome c. (McGill-Montreal Gen. Hosp.
Research Inst., Montreal, Can.). Ann. N.Y. Acad. Sci. 94, 731-40 (1961).
Mostly a review but previously unpublished data on the chromatography
of horse cytochrome c (I) are given. Native I was denatured in 66%
EtOH for 1 hr. and chromatographed on a weak cation-exchange resin col-
umn. Several peaks were obtained and each appeared to represent a homo-
genous substance. As the denatured I peaks came off the column after
native I, it was suggested that they contain more reactive basic groups
indicating varying degrees of disorganization of the native I. From
the review of chromatographic data and low temperature spectra, it was
concluded that there is no evidence for the existence of more than one
mol. form of I in vivo in any single tissue. 57 references.

Marks, Gerald S.
11, 9, 17
CA 65-2621a (1966)

The biosynthesis of heme and chlorophyll. (Univ. Alberta, Edmonton, Can.). Botan. Gaz. 127 (1), 56-94 (1966)(Eng). A review with 189 references, over 50 structural formulae, and a no. of reaction schemes.

Mauzerall, D. and Feher, G.
1, 12, 2
CA 62-4812d (1965)

Optical absorption of porphyrin free radical formed in a reversible photochemical reaction. (Rockefeller Inst., New York, N.Y.). Biochim. Biophys. Acta 88 (3), 658-60 (1964)(Eng). The optical spectrum of the porphyrin free radical was established as the free radical observed in E.S.R. expts. (CA 61, 2111e). The electronic structure of the free radical can be created by either an addn. of the electron to the porphyrin ring forming P^- or removing one electron from phlorin forming PH.

Mauzerall, D. and Feher, G.
16, 2
CA 61-2111e (1964)

Photoinduced porphyrin free radical by electron spin resonance. (Rockefeller Inst., New York, N.Y.). Biochim. Biophys. Acta 79 (2), 430-2 (1964)(in English). Illumination of various porphyrins (P) (uroporphyrins (U), coproporphyrin III (C), and 2,4-di(α,β-dihydroxy) ethyldeuteroporphyrin IX (D)) in the presence of various reducing agents (R) (EDTA, sparteine, NADH, thiazolidine 4-carboxylic acid) results in the formation of free radicals.

Mauzerall, D.
1, 2
CA 63-10226b (1965)

Spectra of molecular complexes of porphyrins in aqueous solution. (Rockefeller Ins., New York, N.Y.). Biochemistry 4(9), 1801-10 (1965) (Eng). The changes in the absorption and emission spectra of porphyrins in various mol. complexes in aq. soln. were studied. These complexes are formed with a variety of mols. including large org. cations and planar neutral heterocyclic mols. Spectral analysis by the method of continuous variation, the lack of isosbestic points, and a new analysis based on band widths all point to the formation of a series of complexes with several addends clustered about the porphyrin ring. Ionic and dispersion forces contribute to the stability of the complexes, but the water structure about these large hydrophobic mols. is an equally important factor. An est. of the latter interaction based on interfacial

7129-Final

tension is given. The spectral changes, particularly the broadening of the Soret band and not of the red band I, are interpreted as a change in the nearly degenerate x and y components of the energy levels, and a model of the complex is derived. Studies at extreme diln. ($10^{-8}M$), an analysis of the optical effects of aggregation on the spectra, and the absence of polarization of fluorescence all favor the view that the uroporphyrin is monomolecularly dispersed. A suggestion is made that such complexes occur in heme proteins as part of the phosphorylating mechanism and that the widespread occurrence of heterocyclic mols. in biol. systems is related to the formation of complexes.

McCartin, P. 1, 17
CA 59-5949c (1963)

Influence of water on the Soret band of chlorophylls. (Univ. of Minnesota, Minneapolis). J. Phys. Chem. 67, 513-15 (1963). The addn. of H_2O to solns. of chlorophylls a and b in dry pyridine reduces the height of the main Soret band and shifts it toward shorter wavelengths. This change is about half complete in 5% aq. solns., and complete in 50% aq. solns. When solns. of chlorophyll a or b in 15% aq. pyridine were cooled to $-55°$, the spectral characteristics of solns. of the pigments in dry pyridine were restored. The principal red bands of both pigments were also decreased in the presence of H_2O, but not so much as was the Soret band. The height of the violet shoulder on the Soret band was almost independent of solvent compn., while the satellite at 638 $m\mu$ was suppressed and the peak at 619 $m\mu$ was enhanced in the presence of H_2O. This interaction between chlorophylls and large amts. of H_2O is distinct from the process of fluorescence activation by traces of activators in such solvents as dry benzene.

McLeod, G. C. 1, 12
CA 55-10612h (1961)

Action spectra of light-saturated photosynthesis. (Carnegie Inst., Stanford, Calif.). Plant Physiol. 36, 114-17(1961). The results with 3 algae showed that at light saturation the rate of photosynthesis depended on wavelength. With Chlorella pyrenoidosa, contg. chlorophyll a (I), the accessory carotenoid pigments (II) and chlorophyll b (III), there was a peak at 440 $m\mu$ and a secondary peak at 650. With Phormidium persicinum, contg. I, II and phycobilins but not III, the peak was at 550-615. With Botrydiopsis alpina, which contains I and II but not III, peaks were at 420 and 695 $m\mu$.

Mel'nikov, S. and Evstigneev, V. B.

Isolation and spectral properties of chlorophyll. (A. N. Bakh Inst.
Biochem., Moscow). Biofizika 9 (4), 414-22 (1964). With Me_2CO-0.04N
NH_4OH (4:1) as extg. agent, the best yield of chlorophyll c (I) was
obtained from dried Cystoseira barbata, Fucus vesiculosus, and
Phaeodactylum tricornutum. Exts. were washed with petr. ether, ad-
justed to pH 5-6 with NaH_2PO_4, satd. with NaCl, and extd. with Et_2O.
Et_2O-extd. 3 isomers of I and pheophytin c (II) were sepd. by paper
chromatography with naphtha petr. ether-iso-PrOH (5:1:0.5). Chroma-
tography was repeated with P. tricornutum exts. for better sepn.
Spots of I and II were eluted with 80% Me_2CO, Et_2O, MeOH, EtOH, BuOH,
iso-PrOH, BuOH, C_6H_6 xylene, toluene, pyridine, or $CHCl_3$. Red hexagonal
crystals were sepd. from an 85% EtOH soln. of I when left overnight
in the dark. I in Me_2CO is emerald-green and gives a strong bright-
red fluorescence. Equal vols. of ether-iodine soln. and 30% KOH give
a red ring between the 2 phases. Spectra of I and II solns. (solvent,
$\lambda_{max.}$ of I in mμ, $\lambda_{max.}$ of II in mμ are: Et_2O, 446-7.5, 426; Me_2-CO,
448, 428; $CHCl_3$, 458, 436; xylene, 456, 436; 80% Me_2CO, 446, -; MeOH,
448, -; EtOH, 445, -; C_6H_6 457, -, toluene 458, -. Fluorescence max.
of I and II solns. (solvent, $\lambda_{max.}$ in mμ of I, $\lambda_{max.}$ in mμ of II) are:
Et_2O, 626, 670; Me_2CO; 631, 672; MeOH, 644, 672; EtOH, 642, 672; C_6H_6,
640, 674; $CHCl_3$, 642, 672; toluene, 639, 675; xylene 638, 676; H_2O, -,
676. In soln., I exists in an assocd. form. Dried I, dissolved in
anhyd. Et_2O is dissocd. and has $\lambda_{max.}$ at 665 and 580 mμ.

Metzner, Helmut

Spectrophotometric measurements with freeze-dried cells of Chlorella.
(Univ. Tuebingen, W. Ger.). Studies Microalgae Photosyn. Bacteria,
Collection Papers 1963, 227-37 (in German). A new method is described
for detg. the absorption spectra for light-scattering materials in a
Zeiss spectrophotometer PMQ II. Freeze-dried cells of C. pyrenoidosa,
as a fluffy dark-green powder pressed into a tablet, produced 9 different
max. and shoulders in the long wavelength band of chlorophyll a (640-
680 mμ).

Mirsky, Rhona and George, P.

Optical rotatory dispersion spectra of cytochrome c and polymers. Univ.
of Pennsylvania, Philadelphia). Proc. Natl. Acad. Sci. U.S. 56 (1),
222-9 (1966)(Eng). The optical rotatory dispersion (ORD) spectra of cyto-
chrome c and its polymers varied widely under different conditions of

pH and ionic strength over a large spectral range. Differences were larger than those in the optical spectra, providing greater sensitivity with ORD as a method for correlating changes in protein structure with changes in the environment of the heme. Specific ion effects were observed at pH 2.2 in ferricytochrome c, and, at pH extremes, the ionic strength of the soln. affected the depth of the 233 mμ trough. The ferrocytochrome c ORD was unaltered over a wide pH range.

Morell, D., Barrett, J., Clezy, P.   9, 11, 13
and Lemberg, R.   CA 58-14344b (1963)

Isolation, purification, and properties of hemin a. (Roy. North Shore Hosp., Sydney). Haematin Enzymes, Symp. Inter. Union Biochem., Canberra, 1959, 1, 320-34 (Pub. 1961). A method is described for the prepn. of unaltered porphyrin a and hemin a from heart muscle. The prosthetic group of cytochromes a, a$_1$, and a$_3$ is heme a. Spectroscopic properties of heme a compds. with nitrogenous bases, CN$^-$, native and denatured proteins and their CO compds. are described and compared with the properties of cytochromes a, a$_1$, and a$_3$. Detns. of heme a content of tissues as porphyrin a or as pyridine hemochromogen a are reported.

Moser, Frank H. and Thomas, Arthur L.   4
                                              CA 60-15105g (1964)

Phthalocyanine compounds. (Std. Ultramarine & Color Co., Huntington, W. Va.). J. Chem. Educ. 41 (5), 245-9 (1964). A review with 29 references.

Moser, Frank H. and Thomas, Arthur L.   4
                                              CA 58-14155h (1963)

Phthalocyanine Compounds. ACS Monograph 157. New York: Reinhold Pub. Corp. 1963. 365 pp.

Mulliken, Robert S.   1, 11
                                              CA 46-5434a (1952)

Molecular compounds and their spectra. II. (Univ. of Chicago). J. Am. Chem. Soc. 74, 811-24 (1952); cf. C.A. 44, 5211f; 45, 7414h. A quantum-mech. theory is presented for the interaction of electron acceptors and donors (Lewis acids and bases) to form 1:1 or n:1 mol. compds. ranging from loose complexes to stable compds. The theory involves resonance between no-bond structures (A, B) and dative structures (A$^-$ -B$^+$), where

A and B are acceptor and donor, resp., atoms, mols., or ions. Two classes of donors (π and onium bases) and 3 classes of acceptors (π, vacant-orbital, and dissociative) are considered particularly, and ionic donors and acceptors are mentioned. A special class of intense electronic absorption spectra characteristic of mol. compds. A.B, and nonexistent for either partner A or B alone, is predicted. The forces which lead to complex-formation (charge-transfer forces) may be of comparable importance to London's dispersion forces in accounting for van der Waals attractions. They have characteristic specific orientational properties of possible importance for the manner of packing of mols. in liquids, in mol. crystals, in heterogeneous systems, and in biol. systems. They may also be important in adsorption. They should increase under compression and thus contribute to compressibilities. The effect of charge-transfer forces in lowering activation barriers for chem. reactions is discussed. The benzene-I and the $BX_3.NR_3$ types of mol. compds. and the Ag^+ complexes are considered.

Mullins, John A., Adler, Alan D.   1, 2
and   Hochstrasser, Robin M.   CA 64-5950h (1966)

Vapor spectra of porphyrins. (Univ. of Pennsylvania, Philadelphia). J. Chem. Phys. 43 (7), 2548-50 (1965)(Eng). Most porphyrin-like materials tend to aggregate, even in relatively polar media. This aggregation, or specific solvent-solute interaction, which can contribute significantly to the spectral location of rather strong absorption bands, has been investigated by a comparison of the soln. spectra in benzene with the vapor spectra of 2 well-known synthetic porphyrins, meso-tetraphenylporphyrin (TPP) and copper TPP (Cu TPP). The soln. spectra of TPP and of Cu TPP in benzene exhibit 2 principal absorbing regions, the Soret region, peaking at 4180 A. for TPP and at 4160 A. for Cu TPP, and visible absorption consisting of 5 bands in TPP (6490, 5920, 5480, 5150, and 4830 A.) and of 4 bands for Cu TPP (6150, 5750, 5380, and 5050 A.). In the vapor spectra, the Soret absorption was detectable above 300°, although the spectra were very broad at 300-500°. The Soret bands of both TPP and Cu TPP were at higher energies in the vapor as compared with benzene soln. spectra, the shifts being 780 and 760 cm.$^{-1}$ in TPP and Cu TPP resp. Only 3 bands were found in the visible absorption of TPP: 5920 A. (weak), 5370 (medium), and 5070 (strong). The 1st (weak) band is thus shifted by ±40 cm.$^{-1}$ in going to benzene soln. while the 2 stronger bands are red shifted in benzene by 350 and 280 cm.$^{-1}$ By using observed optical ds. at 2 temps. and assuming the Clausius-Clapeyron equation in the form $d = d$ $(\ln D)/d(1/T) = L_8/R$, the estd. heat of sublimation is calcd. to be 2×10^4 cal/mole.

Myl'nikov, V. S. and Putseiko, E. K.

1, 4
57-4162g (1962)

Influence of crystal structure on optical and photoelectric properties of phthalocyanines without a metal. (S. I. Vavilov State Optical Inst., Leningrad). Fiz. Tverd. Tela 4, 772-9 (1962). Influence of crystal structure on absorption spectra, photo-e.m.f., and photocond., as well as the sign of photocurrent in layers sublimed in vacuum and powders of phthalocyanine with a metal, was investigated. To 2 different cryst. α and β forms of the pigment correspond different absorption and photoeffect curves in the visible region of the spectrum. In the β-form, which has a denser packing of mols., electronic cond., due apparently to the overlapping of intermol. potential barriers, is observed.

Nekrasov, L. I. and Kapler, R.

13, 17
CA 64-14481b (1966)

Adsorption of chlorophylls a and b on powderlike polyacrylonitrile. (M.V. Lomonosov State Univ., Moscow). Biofizika 11 (1), 48-53 (1966) (Russ). The natural mixt. of chlorophylls a (I) (concn. 0-728 micromole/l.) dissolved in isooctane-PrOH (185:15) was adsorbed on powderlike polyacrylonitrile (III) at 18°. Spectra of diffuse reflection, luminescence spectra, and a photosensitization effect of the in vacuo dried samples on the redn. of methyl red by ascorbic acid were detd. The observed adsorption isotherms were composed of 2 steps. The measured parameters with exception of luminescence intensity changed in each of the 2 parts of the adsorption isotherm in the same way that they changed in the course of a single-step adsorption isotherm. The coeff. of diffuse reflection sharply decreased, the absorbance and the photosensitization effect increased in the beginning of each step of the adsorption isotherm, then all parameters level off. Each step of the adsorption isotherm seemed to correspond to sep. adsorption on cryst. and amorphous regions of the heterogeneous surface of III. Also, the properties of adsorbed chlorophylls were detd. by the sum of properties of I and II adsorbed on different regions of the III surface.

Nekrasov, L. I., et al

16, 17
CA 56-964e (1962)

Magnetic and optical properties of adsorbed chlorophyll (Univ., Moscow). Vestnik Moskov. Ser. II, Khim. 16, No. 2, 9-11 (1961). The adsorption isotherm of natural chlorophyll (in alc. soln.) on silica and alumina gel is a 2-step curve, the 2nd step beginning at adsorbate concn. of about 0.5 μmoles/g. The magnetic susceptibility of chlorophyll adsorbed on alumina gel through a min. at the same concn., while the curves show diffuse reflectance and brightness coeffs. vs. concn. (chlorophyll adsorbed on alumina gel or paper) changed more abruptly.

Okunuki, K.   11, 5
                                                     CA 66-189b (1966)

Cytochromes and cytochrome oxidase. (Univ. Osaka, Japan).
Comprehensive Biochem. 14, 232-308 (1966)(Eng). A review with con-
clusions. Considered are isolation, purification, and properties of
cytochromes, and properties of cytochrome oxidase. 174 references.

Okunuki, Kazuo, Sekuzu, Ichiro,   11, 5
Yonetani, Takashi and Takemori, Shigeki   CA 53-4369c (1953)

Cytochrome a. I. Extraction, purification, and some properties of
cytochrome a. (Osaka Univ.). J. Biochem. (Tokyo) 45, 847-54 (1958).

Olson, Rodney A.   15, 17, 12
                                                     CA 59-1964c (1963)

Transient fluorescence changes in chloroplasts during the photochemical
bleaching of chlorophyll in vivo. (Natl. Inst. of Arthritis & Metabolic
Diseases, Bethesda, Md.). Proc. Intern. Congr. Photobiol., 3rd,
Copenhagen 1960, 473-6 (Pub. 1961). Cryst. purified chlorophyll a was
dissolved in pyridine and adsorbed on activated silica gel. The 4358
A. region from a 200 w. Hg arc was used as the exciting light. The
gel particles (av. diam. 150μ) initially showed a bright red fluorescence.
This was replaced rapidly in air by a bright yellow emission which
gradually disappeared upon continued excitation. These effects are
similar to those observed with chloroplasts under similar optical con-
ditions.

Orten, James M.   2, 13
                                                     CA 51-3686d

Formation and significance of the porphyrins. (Wayne State Univ.,
Detroit). Record Chem. Prog. (Kresge-Hooker Sci. Lib.) 17, 259-66
(1956). Review with 20 references.

Osnitskaya, L. K.   12
                                                     CA 63-8763f (1965)

Photosynthetic development of purple sulfur bacteria, Chromatium
vinosum, within narrow ranges of the spectrum. (Inst. Microbiol.,
Moscow). Mikrobiologiya 34 (2), 204-8 (1965) (Russ); cf. ibid. (1),
19-23. C. vinosum was grown in a mineral medium irradiated with nearly
monochromatic light of the wavelength corresponding to the absorption

maximums of main pigments of this microorganism. The photosynthetic development goes on only at the expense of light at 447, 464, 497, and 535 mμ, which corresponds to the absorption range of carotenoid pigments. This confirms their participation in photoassimilation of CO_2.

Oster, G., Bellin, J. S.   13, 8
and Holmstrom, B.   CA 57-7593b (1962)

Photochemistry of riboflavine. (Polytech. Inst., Brooklyn., N.Y.).
Experientia 18, 249-53 (1962). A review with 58 references.

Oster, G., and Broyde, S. B.   17, 13, 11
                                                  CA 61-3420g (1964)

Chlorophyllin: its analogies with chlorophyll and its possibilities
as a photosynthetic model. (Polytech. Inst. of Brooklyn, Brooklyn,
N.Y.). Ibid. 137-43, discussion 143-4 (in English). The binding of
chlorophyllin a to poly (vinylpyrrolidone) (PVP) at pH 7.0 results
in a shift of its red absorption max. from 640 to 660 mμ. The micro-
crystn. aggregates, absorbing at 735 mμ, yield dimers, absorbing at
688 mμ, when extd. by $CHCl_3$. Dimers may also be produced directly
from PVP-bound chlorophyllin on standing (accelerated by light) and
will revert to the monomers on addn. of alkali. The binding of
chlorophyllin to PVP increases the quantum yield in the photooxidn.
of azo dyes (with ascorbic acid as H-donor). The Krasnovsky reaction
(substrate not stated) in aq. buffer with a "few percent" of pyridine
occurs only in red (not blue) light, and binding to PVP does not
affect the quantum yield. Chlorophyll was found to be a sensitizer
for the decompn. of peroxides, a reaction which may be involved in
O evolution in photosynthesis.

Perkins, H. and Roberts, D. W. A.   1, 17
                                                  CA 60-8268g (1964)

The relative intensities of the blue and red absorption bands of
chlorophyll a. (Canada Agr. Res. Sta., Lethbridge). Biochim. Biophys.
Acta 79 (1), 20-9 (1964) (in English). Recent suggestions that the ratio
of the heights of the 430 mμ and 660 mμ absorption bands of chlorophyll
a in diethyl ether solution should be 1.17-1.19 are not compatible with
our results for the specific activities or the spectroscopic properties
of rigorously purified samples of [1]C-labeled chlorophyll a. It is
possible to obtain values of this ratio significantly lower than the
commonly accepted value of 1.31-1.32 as the result of interaction of
the pigment mols. with alc. or water in the diethyl ether. The lower
values do not reflect improved freedom of the chlorophyll a prepns.
from xanthophylls. A limiting value for this ratio must exist and
this value is 1.29.

Person, Philip and Zipper, Herbert   1, 5
                                                      CA 62-6738d (1965)

Shift of cytochrome oxidase α-peak from 603-605 mμ to 590 mμ by heat
denaturation. (Veterans Admin. Hosp., Brooklyn, N.Y.). Biochim.
Biophys. Acta 92 (3), 605-7 (1964)(Eng.). When prepns. contg. cyto-
chrome oxidase were heated, characteristic and reproducible changes
occurred in the α-peak of the oxidase. As temp. was increased, the
α-peak at 603-605 mμ was lowered, broadened, and shifted in sequential
fashion to the 590-mμ region. The nonheat-treated control prepn.
(25°) had a typical oxidase α-peak at 603-605 mμ. With exposure to
elevated temps. (45, 50, and 60°), the α-peak was sequentially lowered,
its max. was broadened, and it moved to shorter wavelengths. Finally,
after 5 min. at 60°, the α-peak was transformed into a lower, broad
max. centered at 590 mμ. The shift from 603 mμ to 590 mμ occurred in
stages as the temp. was elevated and was not an abrupt transition.
This same pattern of change in the max. was observed in all prepns.
thus far tested, i.e., isolated yeast and beef-heart-muscle mitochondria,
and deoxycholate solubilized oxidase prepns. from yeast and beef heart.
In the Soret region of the control prepn. (25°), there is a skewing of
the curve in the region of 444 mμ, belonging to the oxidase. With
increase in temp. the intensity of the entire Soret absorbance in this
region falls, the specific changes cannot be isolated in the oxidase
Soret peak. The above spectral changes were accompanied by losses of
oxidase activity; e.g., exposure for 5 min. at temps. below 45° did not
produce significant inactivations; after 5 min. at 45°, inactivations
of 30-50% were measured; following 5-min. exposure at 55-60°, 80-100%
loss of activity resulted. Usually, when the α-max. of a given prepn.
shifted from 603-605 mμ to 600 mμ or below, the activity of the prepn.
was very low or completely lost.

Personov, R.   1, 4
                                                      CA 59-9475b (1963)

Linear emission and absorption spectra of phthalocyanine in frozen
crystalline solutions. Optika i Spektroskopiya 15 (1), 61-71 (1963).
The absorption and fluorescence spectra were investigated of phthalo-
cyanine (I) in octane, nonane, and decane at 77°K, with an ISP-67
spectrograph and excitation from a Xe lamp with a green-blue filter
(transmission region 3600-6200 A.). Under these conditions, the ob-
tained spectra were well defined and consisted of narrow bands. Mea-
surements of spectral wavelengths were made with a precision of ±1-2 A.
The obtained linear spectra of I indicate the appearance of 2 electron
transitions at 6910 and 6530 A. Each transition contained a large no.
of vibrational sublevels. 20 references.

Pestemer, M.   1
                                                CA 64-10633c (1966)

Anleitung zum Messen von Absorptionsspektrum Ultraviolett und Sichtbaren
(Introduction to the Measurement of Absorption Spectra in Ultraviolet
and Visible Light). Stuttgart: G. Thieme. 1964. 230 pp. DM 7.80.

Phillips, John P.   1, 13
                                                CA 61-6560d (1964)

Spectra-Structure Correlation. New York. Academic Press. 1964.
172 pp. $6.00.

Platt, John R.   2, 13
                                                CA 50-7196f (1956)

Electronic structure and excitation of polyenes and porphyrins.
(Univ. of Chicago). Ibid. 71-123.

Pringsheim, Peter   15

Fluorescence and Phosphorescence. Interscience Publishers, Inc., New
York (1949) p. 425-432.

Pullman, Bernard, et al   2, 5, 13
                                                CA 55-96b (1961)

Features of the electronic structure of the iron-porphyrin complexes
with special reference to the oxidoreductive properties of cytochromes.
(Univ. Paris). Proc. Natl. Acad. Sci. U.S. 46, 1011-20 (1960). Mol.
orbitals are detd. which may establish themselves between the electronic
orbitals of the porphyrin ring and those of the metal cation. Energies
of mol. orbitals in the porphin ring, and in ionic and covalent ferri-
and ferroporphyrins are listed and discussed with emphasis on the values
of the energies of the π orbitals, and on those of the highest occupied
and lowest empty of these orbitals. The distribution of the mobile
electronic charges in the different types of complexes is illustrated;
this gives complementary information on the differences of the structure
between the 2 types of Fe-porphyrin complexes, and on the nature of the
interaction between the porphyrin and the Fe electrons in the cytochromes.

Putseiko, E. K. and Terenin, A. N.   1, 17
                                                  CA 55-17775c (1961)

Photoelectric sensitivity of crystalline, chlorophyll and green-leaf
pigments. Doklady Akad. Nauk S.S.S.R. 136, 1223-6 (1961); c.f. CA
55, 8064f. Cryst. layers of chlorophyll (a or a + b) and correspond-
ing methylchlorophyllides were examd. as to spectral distribution of
the photoelec. emission after activation by heating in H_2O vapor at
50°. The red max. was gradually displaced toward longer wavelengths
by treatment with H_2O vapor. Chlorophyll a showed a narrower photo-
elec. e.m.f. max. than chlorophyll a + b, and showed the same be-
havior to H_2O vapor as described above. Pigments of green leaves of
nettle (Urtica dioica) and Philadelphus (a mixt. of chlorophylls,
carotenes, and lipoproteins) showed a much smaller lag of the photo-
elec. current than was displayed by the individual pigments above and
the increase in current occurred in less than 1 sec. The spectral
max. in these cases were at 710-20 mμ, indicating the presence of
cryst. chlorophyll; the 420 mμ max. in these pigments was much greater
than the 720 mμ max., which was not observed for isolated pigment.
In the regions of both max. the photocurrent carriers showed a pos.
charge.

Rabinowitch, Eugene and Govindjee, Rajni   17, 13
                                                  CA 55-13485f (1961)

Different forms of chlorophyll a in vivo and their photochemical
function. (Univ. of Illinois, Urbana). Ibid 378-86. IN: Symposium
on Light and Life, Johns Hopkins University, 1960, Light and Life;
proceedings. Edited by William D. McElroy and Bentley Glass. (Johns
Hopkins University. McCollum-Pratt Institute. Contribution No. 302.)

Rabinowitch, Eugene   12
                                                  CA 50-14062g (1956)

Photosynthesis and Related Processes. Vol. II. Pt. 2. Kinetics of
Photosynthesis, (continued); Addenda to Vol. I and II. Pt. 2. New
York: Interscience Pubs. 1956. 896 pp. $18.50. Cf. C.A. 49, 12623e.

Rabinowitch, Eugene I.   12, 1
                                                  CA 54-14378f (1960)

Primary photochemical and photophysical processes in photosynthesis.
(Univ. of Illinois, Urbana). Discussions Faraday Soc. No. 27, 161-
72 (1959). The structure of chloroplasts and the optical properties

of chlorophyll are examd. from the point of view of possible migration
of excitons and sepn. of charges after light absorption in a chlorophyll
mol. Evidence suggests the presence in chloroplasts of noncryst.
monomol. chlorophyll layers. It also appears that the chlorophyll mols.
are present in (at least) two different states. Resonance migration of
excitation energy of 100-200 chlorophyll mols. appears plausible; per-
haps these are mols. attached to a single globular protein mol. in
the chloroplast lamellae. There is no spectroscopic evidence for the
presence of electron conductance levels; arguments for their existence,
derived from paramagnetic resonance expts., do not seem convincing.
Evidence suggesting that chlorophyll mols. undergo reversible trans-
formations (perhaps involving a redn.) in photosynthesis is discussed;
the 2 types of chlorophyll present in chloroplasts may be involved in 2
different steps of the primary photochem. process.

Radda, G. K. and Calvin, Melvin   13, 8
                                                   CA 60-9511h (1964)

Chemical and photochemical reductions of flavine nucleotides and
analogs. (Univ. of California, Berkeley). Biochemistry 3 (3),
384-93 (1964). The anaerobic photoredn. of riboflavine, flavine
mononucleotide (FMN), 6, 7-dimethyl-9-hydroxyethylisoalloxazine,
and lumiflavine in the absence of electron donors is studied. Lumi-
flavine, unlike the other 3 compds, does not undergo photobleaching.

Rafaeloff, R., Kohl, F. J., Krueger, P.C.
and Kenney, M. E.

4
CA 65-3303a (1966)

New Group IV phthalocyanines. (Case Inst. of Technol., Cleveland, Ohio).
J. Inorg. Nucl. Chem. 28 (3), 899-902 (1966).

Randolph, M. L.   16, 11

Quantitative Studies of Electron Spin Resonance Produced in Biologically
Significant Materials by Ionizing Radiations, Free Radicals in Biological
Systems (1961) p. 249-261.

Rikireva, G., et al   16, 17
CA 62-5489h (1965)

Electron paramagnetic resonance of chlorophyll's triplet state. (A. N.
Bakh Biochem. Inst., Moscow). Dokl. Akad. Nauk SSSR 159(1), 196-7 (1964)
(Russ); cf. Biofizika 8(5), 550 (1963). E.P.R. signals near 1600 oe.
were found on illumination in the visible of frozen alc. sqlns. of
chlorophylls(a + b)(I) and b (II) at 77°K. with a 3-cm. spectrometer
and were identified with the triplet state. Chlorophyll a (III) did
not show the signal. With I and II, concn. quenching of the signal
occurred at concns. above 10^{-2}M. A signal at 3300 oc. was found after
10-30 sec. illumination above 370 mµ with I, II, and III, decaying very
slowly in the dark and was identified with the free electron, with an
amplitude dependence on the square of the illumination. This signal is
thought to result from a photooxidn. of the pigment or reduction of the
solvent.

Rimington, C.   1, 2
CA 54-18881a (1960)

Spectral-absorption coefficients of some porphyrins in the Soret-band
region. (Univ. Coll. Hosp. Med. School, London). Biochem. J. 75,
620-3 (1960). The spectral absorption in the Soret region of some
common porphyrins has been examd. Values are reported for the extinction
coeffs. at the Soret band of the esters in neutral solvent and of the
porphyrins dissolved in acid of suitable concn. The molar extinction
coeffs. and the Soret max. are as follows: uroporphyrin III octa-Me ester
(syn.) 2.17×10^5, 405-6 mµ; uroporphyrin I octa-Me ester (nat.)--, 406;
coproporphyrin III tetra-Me ester 1.80×10^5, 399.5; etioporphyrin I 1.60×10^5, 399.5; deuteroporphyrin di-Me-ester 1.75×10^5, 399; hematoporphyrin
di-Me-ester--, 402; porphine (neutral) 2.64×10^5, 396.5; phylloerythrine
Me ester 1.95×10^5, 415; protoporphyrin di-Me ester 1.71×10^5, 407.5;
uroporphyrin III (syn.) 5.28×10^5, 405.5; coproporphyrin III 4.89×10^5,

399.5; deuteroporphyrin 4.33×10^5, 389; hematoporphyrin--, 401; porphine (acid) 3.48×10^5, 391; phylloerythrine 2.78×10^5, 421; protoporphyrin 2.62×10^5, 408. Recommended values are also tabulated for use with the formula of R. and Sveinsson (CA 45, 5750g) which permits correction for slight-absorbing contaminants of porphyrins in impure solns.

Rimington, C.   2
CA 50-1111a (1956)

Porphyrins. (Univ. Coll. Hosp. Med. School, London). Endeavour 14, 126-35 (1955). A review of the structures of porphyrins. The biosynthesis of porphyrins and of hem is surveyed. The mechanism of degradation of hemin is illustrated. The role of uroporphyrin, coproporphyrin, and protoporphyrin in the biosynthetic pathway leading to hem is discussed.

Rimington, C.   9, 2
CA 51-18041e (1957)

Hem pigments and porphyrins. (Univ. Coll. Hosp. Med. School, London). Ann. Rev. Biochem. 26, 561-86 (1957); cf. C.A. 44, 10765b; 50, 1111a. A review of advances since 1950 with emphasis on developments of 1956, and covering porphyrin and pyrrole chemistry, analytical methods, biosynthesis, porphyria, and porphyrinuria. 262 references.

Rimington, C., and Kennedy, G.   2
CA 58-689d (1963)

Porphyrins: structure, distribution, and metabolism. (Univ. Coll. Hosp. Med. School, London).

Ringer, A.   1, 13
CA 45-10053g (1951)

Measurement of absorption in solutions of green, blue and violet dyes. (Kornmarkt 3, Mühlhausen/Thür., Ger.). Pharmazie 6, 44-8, 103-7, 156-61 (1951); cf. C.A. 45, 2632b. The following are discussed and absorption curves (step photometer) and max. given: $Cr_2(SO_4)_3 12 H_2O$, Cr peroxide, Na cupritartrate, $KMnO_4$, I, Nd, Guinea Green B, Alizarinecyanine Green G extra, bromophenol blue, bromothymol blue, thymolphthalein, methylene blue, Thionine Blue GO, Giemsa stain, May-Grünwald stain, Victoria Blue R, Victoria Blue 4R, Patent Blue V, Aniline Blue, methyl violet, Diamine Black BH, Chicago Blue, Diamine Blue 3B, Dianil Blue B, phthalocyanine, indigo, Indanthrene Blue RS, Brilliant Indigo BASF/B, and coloring matters from Alkanna tinctoria, Delphinium consolida, and Althaea rosea.

Ringer, A.   1, 17
                                          CA 44-7146f (1950)

Light absorption of solutions of green coloring matters. Pharmazie
3, 247-51 (1948).--Absorption spectra readily distinguish between
chlorophyll, green inorg. salts, and green dyes in soln.
The effect of vibrational coupling on the reactivity of hydrocarbons.
A. R. Ubbelohde. Rev. inst. franc. petrole 4, 488-501 (1949). Two
processes have been suggested in explanation of the comparative reactivity
of homologs and isomers. According to the electronic theory, neighbor-
ing groups may affect the energies of electrons taking part in a bond.
According to the vibration coupling theory the vibrations of neighboring
groups may interact in varying degree with the vibrations of a given
bond. Recent phys. data on hydrocarbons are reviewed in an attempt to
assess the relative importance of the two processes in the oxidation
of homologs and isomers. Vibration coupling seems to be of particular
importance in hydrocarbon oxidations, where the reactivity increases
with increasing length of the C chain.

Robinson, G. Wilse   1, 13
                                          CA 55-20611d (1961)

Spectra and energy-transfer phenomena in crystalline rare-gas solvents.
(California Inst. of Technol., Pasadena). J. Mol. Spectroscopy 6,
58-83 (1961). The use of cryst. nonpolar gases at 4.2°K. as solvents
allows a study of spectra, solvent shifts, and energy transfer phenomena
over a wide range of solvent properties. Contributions to the spectral
shifts can arise from the usual London dispersion energy, exchange
repulsions and attractions, and dipole-induced dipole interactions.
Except for the frequency shifts and certain intensity perturbations,
the spectrum of a nonpolar solute in this sort of an environment is like
that of a randomly oriented gas at 4.2°K. A striking perturbation on
the phosphorescence lifetime of C_6H_6 in heavy rare gases was explained
on the basis of an exchange interaction mixing states of the C_6H_6-rare
gas complex, with Russell-Saunders components further mixed by the large
rare-gas spin-orbit perturbation. The oscillator strength for the purely
radiative $^3B_{1u}$-$^1A_{1g}$ transition in unperturbed C_6H_6 is 7.7 x 10^{-11}, and a
150-cm. path of highly purified liquid C_6H_6 should be sufficient to
observe in absorption the 1st strong band of this system predicted to
lie near 31,000 cm.$^{-1}$ A type of tunnelling from the lowest triplet state
back to the ground singlet state was found. It usually involves high
vibrational quantum nos. of the ground state. Energy transfer from the
excited singlet to the excited triplet was highly sensitive to local
solvent environment. This process apparently can be essentially stopped
or made 100% efficient simply by changing the mass of the solvent mols.
This phenomenon is no doubt a function of the strength of the coupling
between the internal modes and the lattice modes, the coupling being

7129-Final   190

dependent on the polarizability of the solvent. Solid H or Ne solvents should provide the least opportunity for energy transfer during an electronic lifetime. Very polarizable solvents promote the population of the lowest triplet state in those cases where the nonradiative process is slow in hydrocarbon solvents.

Salum, Yamil, et al
1, 2
CA 57-5474g (1962)

Spectrophotometric studies on porphyrins. (Univ. Buenos Aires). Anales Asoc. Quim. Arg. 49, 269-78 (1961). The visible spectral curves of uroporphyrin I (I), uroporphyrin III (II), and phyriaporphyrin III (III) in dil. HCl and their Me esters in $CHCl_3$ are reported. The Soret bands in 0.5N HCl ($\epsilon \times 10^{-5}$ in parenthesis) were: I 405.5 (5.40), II 405.5 (4.80), and III 404.5 (4.95).

Sauer, Kenneth
18, 17
CA 63-3225b (1965)

Optical rotatory dispersion of chlorophyll in solution and in chloroplast subunits. (Univ. of California, Berkeley). Proc. Natl. Acad. Sci. U.S. 53(4), 716-22 (1965) (Eng). Quantasome aggregates were prepd. from sonicated spinach chloroplasts, and chlorophyll a was sepd. chromatographically. The optical rotatory dispersion spectrum of the aggregates showed strong Cotton effects assocd. with absorption bands in the red and blue regions. The chlorophyll in CCl_4 solns. showed changes in its dispersion spectrum with changing concn. and large Cotton effects at high concns. where chlorophyll dimers were stable. The observed dispersions in quantasomes were interpreted to arise from strong interactions among aggregated pigment mols. in their lipoprotein matrix.

Savinov, B. G.
3, 1
CA 54-626e (1960)

Spectrophotometric testing in a series of carotene dyes. Primenenie Metodov Spektroskopii v Prom. Prodovol'stven. Tovarov i Sel'sk. Khoz., Leningrad. Gosudarst. Univ. im. A. A. Zhdanova, Materialy Soveshchaniya, Leningrad 1955, 136-44 (pub. 1957); cf. C.A. 50, 7925h. On the basis of the dependence of spectrophotometric characteristic on the stereoconfiguration of a series of carotene dyes, the structure of particular cis-trans isomers could be closely approximated. The ultraviolet spectra of pigments of carotene series, successfully sepd. by chromatography, showed 3 basic max. (mμ) with 2 of them especially accentuated: α-carotene, in H_2S (I), 511, 478, 446, in chloroform (II) 492, 460, 345, in benzene (III) 490, 458, 448, in petr. ether (IV) 478, 447, 425, in

ethanol (V) 479, 449; β-carotene, in I 521, 485, 452, in II 493, 465, 436, in III 498, 464, 424, in IV 484, 451, 426, in V 487, 453; γ-carotene, in I 533, 496, 463, in III 510, 477, 447, in IV 495, 463, 432; kryptoxanthin, in I 518, 483, 453, in II 497, 463, 433, in IV 486, 452, 420; zeaxanthin, in I 518, 483, 450, in II 494, 462, 429, in IV 483, 451; flavoxanthin, in I 478, 448, in II 459, 430, in IV 450, 421; violaxanthin, in I 505, 470, 440, in II 482, 452, 424, in III 484, 454, in IV 472, 443, in III 507, 474, 445, in V 503, 472, 445 mμ, were identified.

Seely, Gilbert R.

Molecular orbital study of the porphyrins. (Univ. of Washington, Seattle). J. Chem. Phys. 27, 125-33 (1957). A L.C.A.O. mol. orbital calcn. was made for models of porphin and its hydrogenated derivs., chlorin, α- and β-tetrahydroporphin, and hexahydroporphin. Application of the results to the spectra of these compds. provided a consistent interpretation in terms of relative energies of the 2 highest filled mol. orbitals. Comparison was made largely with the observed spectra of Zn tetraphenylporphyrins. The calcn. confirms the proposed structural assignments for α- and β-tetrahydroporphins.

Seely, G. R. and Jensen, R. G.

Effect of solvent on the spectrum of chlorophyll. (Charles F. Kettering Res. Lab., Yellow Springs, Ohio). Spectrochim. Acta 21(10), 1835-45 (1965) (Eng). Visible spectra of chlorophyll in 40 solvents were recorded and the following parameters tabulated for each: position of the red and Soret bands, extinction coeff. and half-width of the red band, the Soret/red band and the Soret/Soret satellite band extinction coeff. ratios. The position of the red band depends more on the n than on the dielec. const. Interpretation of other spectral properties is assisted by division of solvents into 3 classes: (1) polar aliphatic compds. with single bonds only; (2) polar aliphatic compds. with multiple bonds; and (3) mainly aromatic compds. With the aid of this division, correlations were found between the half-width and the part of the red shift that depends on dielec. const., between the position of the Soret and red bands, and between the Soret/red and the Soret/ Soret satellite absorptivity ratios.

Sevchenko, A. N., et al

The symmetry of the porphyrin molecules. Doklady Akad. Nauk. S.S.S.R.
128, 510-13 (1959). S., et al. investigated the polarization of
fluorescence of the porphyrins in acid, neutral, and the metal-por-
phyrins to det. its symmetry. The absorbing spectra of the investigated
compds. show the typical porphyrin spectra; the band was only slightly
displaced, owing to the solvent used. The emitted spectra in all the
cases investigated had 2 bands closely sym. to the 2 absorbing bands.
Fluorescence was excited in the uppermost part of the absorption band.
The degree of polarization was measured in the lower part of the
emission band. The optimum polarization was measured by the dependence
of the degree of viscosity. The viscosity was varied by changing the
temp. The limiting polarization was calcd. by extrapolating to
infinite viscosity. The porphyrin mol. investigated was tetraphenyl-
porphyrin, which possesses the same sym. properties as the porphyrin
mol., and so the conclusions drawn on it must be valid for the por-
phyrin mol. From the study of the Zn tetraphenylporphyrin in neutral
soln., S., et al. concluded that the mol. belongs to the D_{4h} symmetry
group. The change in the polarization spectra when the porphyrin is
shifted from the acid to neutral or to metal-porphyrin is conclusive
evidence of the high symmetry of the porphyrin mol.

Sevchenko, A. N., et al

Limiting polarization of the fluorescence of porphyrins. Optika
Spektroskopiya 10, 750-8 (1961).

Sevchenko, A. N.

Spectral luminescent study of porphyrins. Izv. Akad. Nauk SSSR, Ser.
Fiz. 26, 53-60 (1962). A survey of available exptl. data (25 references)
and of new data on the polarization spectra of protoporphyrin in castor
oil shows that the 2 fluorescence bands in porphyrins are due to 2
different oscillators. In the case of a 2-band system (symmetry D_{4h},
metal porphyrins) the 2nd absorption band, and in the case of a 4-band
system (porphyrins) the 2nd and 4th bands, are due to the superposition
of vibrations on excited electronic states. The 2nd emission band is
due to the superposition of the same vibrations on the ground state.
Transitions with a fully symmetric vibration are parallel to the purely
electronic transition; nonsymmetric vibrations are perpendicular to the
electronic transition.

Shakhov, A. A., et al   12
                                               CA 65-5879g (1966)

Ultraviolet irradiation of plants as a problem of space phytophysiology.
Probl. Kosmich. Biol., Akad. Nauk SSSR 4, 474-86 (1965)(Russ). Various
plants were irradiated with short-wave and medium-wave uv-rays at alti-
tudes of 4000-5000 m. (Pamir) and 3200 m. (Mount Aragats). In plants
exposed to uv-rays with a wavelength of 254 mμ, the structure of the
chloroplasts was normal and their pigment content was high, which
indicates considerable resistance to uv-irradiation.

Shakhverdov, P.A.   1, 7
                                              CA 64-12055f (1966)

Triplet-triplet absorption spectra of some tetrapyrrole pigments in
liquid solutions. Optika i Spektroskopiya 19(6), 933-5 (1965)(Russ).
A comparative study was made of the absorption spectra of chlorophyll
derivs. (chlorophyllin, chlorophyllide, theophytin, and theophorbide)
dissolved in C_6H_6, styrene, EtOH, and Me_2CO, under impulse illumination.
The consts. of the rate of deactivation of their triplet states are
tabulated. Significant structural changes in the mols. of tetrapyrrole
pigments, when the system of conjugated bonds is conserved, have little
effect on the triplet-triplet absorption at 400-700 mμ. The effect is
pronounced in the near-ir region.

Shashoua, Victor E.   18, 2, 4
                                             CA 63-12522e (1965)

Magnetooptical rotation spectra of porphyrins and phthalocyanines.
(E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.). J. Am.
Chem. Soc. 87(18), 4044-8 (1965)(Eng). The magnetooptical rotation
(M.O.R.) spectra of a no. of porphyrins, phthalocyanines, and their
metal derivs. were detd. in an effort to correlate M.O.R. spectra with
absorption spectra. Of the compds. studied, Zn and Mg phthalocyanine
had the largest magnetic rotations: -8×10^5 and -8.8×10^5, resp. No
evidence could be obtained for relations between the shape or the
magnitude of the observed magnetic rotations and the ground-state para-
or diamagnetism of the mols. Some evidence was obtained for a relation
between the shape of the M.O.R. spectrum and the polarizations of
transitions in the absorption spectra. A description is given of an
automatic recording M.O.R. spectropolarimeter with a solvent-compensating
feature and a sensitivity of ± 0.001 and $\pm 0.003°$ for the visible and uv
regions, resp., of the spectrum.

Shashoua, Victor E.

Magnetooptical rotation (M.O.R.) spectra of cytochrome c. (E. I. du Pont de Nemours & Co., Wilmington, Del.). Nature 203 (4948), 972-3 (1964). The M.O.R. spectra of both oxidized and reduced cytochrome c show distinctive peaks. The reduced form has 6 neg. peaks corresponding to the α (549 mμ) and β (520 mμ) absorption bands, showing that the latter consists of ≥ 6 fused peaks. The large neg. sp. rotation of -1450 at 549 mμ is decreased to -160 for the oxidized form, suggesting that this band can be used to study the kinetics of the interconversion. In the Soret region, a sp. rotation of -1750 at 410 mμ for the reduced form is only slightly increased on oxidn.

Shiga, I. T. and Piette, L. H.

Triplet state studies of flavine by electron paramagnetic resonance. (Varian Assocs., Palo Alto, Calif.). Photochem. Photobiol. 3(3), 213-22 (1964).

Shul'ga, A. M., Gurinovich, G. P., and
    Sevchenko, A. N.

A study of metal complexes of photoreduced forms of porphyrins and chlorins. (Inst. Phys., Minsk). Dokl. Akad. Nauk SSSR 169(5), 1206-8 (1966)(Russ). Spectral curves were shown for photoredn. of etioporphyrin, chlorin, and chlorophyll in the presence of Zn (OAc)$_2$ with ascorbic acid as the reducing agent. The 525 mμ forms of chlorophyll and pheophytin were identical, confirming a previous hypothesis (Seely and Folkmanis, CA 61).

Sidorov, A. N.

Spectral studies of reversible changes of compounds of the porphin series. Usp. Khim. 35(2), 366-91 (1966)(Russ). A review with 139 references through 1964, dealing with spectroscopic studies of changes in porphins, including isomerization, tautomerism, mol.-complex formation, H exchange hydrogenation, dehydrogenation reactions, and reversible photoredn.

Smith, Lucile, Baltscheffsky, Margareta,   1, 12
    and Olson, J.M.   CA 54-12271a (1960)

Absorption-spectrum changes observed on illumination of aerobic sus-
pensions of photosynthetic bacteria.   (Univ. of Pennsylvania, Phila-
delphia).   J. Biol. Chem. 235, 213-18 (1960); cf. C.A. 53, 19040a;
cf. following abstr.   Illumination of aerobic suspensions of Rhodo-
spirillum rubrum or Rhodopseudomonas spheroides results in 3 kinds of
changes of absorption spectra: (a) Oxidn. of one of the cytochrome
systems.   This is the electron-transport chain over which the photo-
oxidant and photoreductant react coincidentally with the phosphoryla-
tion of adenosinediphosphate (ADP) to adenosinetriphosphate (ATP).
(b) The appearance of a broad absorption peak at 434 mμ.   (c) A
decrease in the carotenoid absorption peaks and the appearance of absorp-
tion peaks at longer wavelengths.   Changes (b) and (c) are always very
small in aerobic bacteria taken directly from a growing culture, but
these are increased when the bacteria are washed or when inhibitors such
as phenylmercuric acetate or cyanide are added.   The conditions for the
appearance of the absorption peak at 434 mμ and a study of the kinetics
of its appearance indicate that it is not formed in normal oxidn.-redn.
reactions after illumination, but appears when electron-transport
reactions are inhibited.

Snart, Ronald S.   13
                                                 CA 62-2927d (1965)

The optical and electrical properties of mitochondrial preparations.
(Indiana Univ., Bloomington).   Biochim. Biophys. Acta 88(3), 502-6 (1964)
(Eng).   It has been shown that electron-acceptor quinones can complex to
proteins, decreasing their elec. resistivity and semiconductive activa-
tion energy.   Such complex proteins are suitable for energy transport
in biol. systems by a semiconduction mechanism.   Coenzyme Q_{10} is known
to be involved in oxidative phosphorylation reactions in assocn. with
the cytochrome system.   The semiconductive and optical properties of a
cytochrome c-coenzyme Q_{10} complex have indicated a possible mechanism
for such reactions and an investigation of this complex in a mitochondrial
lipid medium and complete mitochondria has provided evidence for the
possible role of a semiconductive mechanism in mitochondrial energy
transport.

Solov'ev, K.   1, 15, 2
                                                CA 58-3013e (1963)

Spectroscopic and luminescence relations pertaining to porphin deriva-
tives. Vestsi Akad. Navuk Belarusk. SSR, Ser. Fiz.-Tekhn. Navuk 1962,
No. 3, 27-38. Porphins have a characteristic absorption spectrum con-
sisting of 4 bands. On introduction of a metal into the mol., bands III
and IV disappear. Spectroscopic investigation of the mol. symmetry of
porphyrins by the max. polarization method showed that introduction of a
metal atom increases the symmetry from D_{2h} to D_{4h} and reduces the no. of
bands in the spectrum. A study of the mirror image symmetry between
absorption and fluorescence emission spectra (Levshin effect, Photo-
luminescence of Liquid and Solid Compounds, 1951 (CA 49, 12974f)) on
porphins contg. and not contg. metals indicated that bands I and II
correspond to a single electron transition. This was confirmed by a
calcn. of probabilities of electron transitions accompanied by emission,
which definitely showed that bands I and II are due to one electron
transition and bands III and IV to another. The metal atom produces
a perturbation. A substituent in 1 of the pyrrole rings increases the
perturbation so that the intensity of band I becomes still greater. An
increased nuclear charge of the metal (e.g., Mg → Zn) increases the prob-
ability of an emissionless transition of an excited mol. to a triplet
state and also of a direct deactivation to the ground state. To investi-
gate the intermol. transfer of energy in porphin rings to the central
metal atoms and the effect of the metals on this transfer, Sevchenko,
et al.(CA 55, 12030g) synthesized phthalocyanine complexes contg. rare
earth elements. The complex with Eu had the strongest fluorescence,
that with Gd, which has a very high magnetic moment, exhibited a weaker
fluorescence, and that with Y did not fluoresce at all (the excited level
of Y is lower than that of the phthalocyanine ring, while that of Eu is
higher).

Solov'ev, K. N., et al   1, 2
                                                CA 63-16182c (1965)

Quasi-linear electron spectra of porphine and its derivatives. Tr.
Komis. po Spektroskopii, Akad. Nauk SSSR 1964(1), 634-47 (Russ). The
quasi-linear absorption and luminescence spectra of porphine and dihydro-
porphine, and of some of their derivs. in cryst. matrixes at $77^{\circ}K$. were
studied. The observed frequency differences are interpreted. A com-
parison of the spectra of porphine and chlorine showed that hydrogenation
of the double bond in one of the pyrrole rings did not impair the sharp-
ness of the lines. The absence of splitting in the spectra of chloro-
phyll is due to the complexity of the system of the substituents, and
probably to the presence of phytol group. From Ref. Zh., Fiz. D. Fiz.
Atoma i Molekuly. Optika. Magnitn. Rezonans 1965, Abstr. No. 3D196.

Stanienda, Alfred   17, 13
                                                 CA 63-10228a (1965)

Electrochemical investigations of chlorophylls a and b and of the
pheophytins a and b. (Humboldt-Univ., Berlin). Z. Physik. Chem.
(Leipzig) 229(3/4), 257-72 (1965).

Stern, A. and Molvig, H.   15, 2
                                                 CA 30-2490 (1936)

The fluorescence of the porphyrins. Z. physik. Chem. A175, 38-62
(1935). The fluorescence spectra of several porphyrins in dioxane
were detd. and compared with the absorption spectra. The effects of
various substituted groups were studied and many regularities found
to hold for both spectra. The positions of the fluorescence-band maxima
of individual normal porphyrins are similar to those of the analogous
absorption spectra. The same holds for the direction of the displace-
ment of bands caused by various groups. The main lines and the fore
bands I of the fluorescence spectra lie practically on the same plane
as the red bands and bands Ia of absorption spectra. γ-Substituted
porphyrins and those having both unsatd. and carbonyl groups are ex-
ceptions. Position isomers cannot be distinguished from each other
by their fluorescence spectra. The effect of various substitutions
in the dihydroporphin system was studied and the fluorescence spectra
of various derivs. of α- and β-chlorophyll detd. Regularities were
found although different from those in the case of normal porphyrins.
The fluorescence spectra of 2 solid porphyrins and a metallic deriv.
of a porphyrin are described. The fluorescence spectra of 2 solid
pyrromethenes are given.

Stern, A. and Wenderlein, Hans   1, 2
                                                 CA 30-1657 (1935)

The light absorption of porphyrin. III. Z. physik. Chem. A174, 321-34
(1935); cf. C. A. 30, 382[4]. Comparisons were made of the absorption
curves of 2 chloroporphyrin-e_5 dimethyl esters that are isomers but
differ greatly in structure. The presence of a ring between γ C atom
and position 6 in the ester produced with MeOH-HCl could be confirmed
by comparing its absorption curve with that of rhodoporphyrin-XV
dimethyl ester. The absorption of a porphyrin unsubstituted in the
β-position and with an isocyclic ring was measured and only a small
blue displacement found as compared with that corresponding to β-
position in Et-substituted porphyrin. Various derivs. of the chloro-
phyll-β series were studied and regularities found similar to those
of the α-series. The effect of hydration of vinyl group in the 2-
position upon light absorption in both α- and β-series is discussed.

Stern, A. and Wenderlein, Hans　　　　　　　　1, 2
　　　　　　　　　　　　　　　　　　　　　　CA 30-5500 (1936)

The absorption of light by porphyrins. IV. Z. physik. Chem. A175,
405-37 (1936); cf. C. A. 30, 1657[4]. The light absorptions of por-
phyrins, tetra- and hexa-substituted porphyrins, porphyrins treated
with alcs. of high mol. wt., and porphyrins derivs. contg. one and
two CO groups were measured.

Suvorov, N. I. & Parshina, Z. S.　　　　　　　1, 17, 12, 6
　　　　　　　　　　　　　　　　　　　　　　CA 50-1988f (1956)

Spectrophotometric study of the absorption bands of chlorophyll in
connection with the problems of cosmic evolution of photosynthesis.
Akademiia Nauk Kazokhskoi S.S.R.

Takeyama, Naokata　　　　　　　　　　　　　　12
　　　　　　　　　　　　　　　　　　　　　　CA 55-15628h (1961)

Molecular mechanism of energy transfer and conversion in the photo-
synthetic system. (Kyushu Univ., Fukuoka, Japan). Experientia 17,
43-6 (1961)(in English). An attempt is made to develop a phys. model
for transfer and conversion of excitation energies in photosynthesis.
The main processes consist of energy transfers from accessory pigments
(carotenoids), phycobilins, chlorophyll b, c, etc.) to chlorophyll
a. The energy migrations in the aggregate system of chlorophyll-a mols.
is explained by the intramol. "exciton" of Forster (CA 43, 5667d).
Energy exchange by stimulation of a π-π triplet of chlorophyll through
a paramagnetic metal-contg. enzyme is proposed and discussed.

Terenin, A. N., Tachin, V. and Shakhverdov, P.　13, 8
　　　　　　　　　　　　　　　　　　　　　　CA 63-15738b (1965)

Spectra of transients of riboflavine, lumiflavine, and lumichrome under
flash excitation. (State Univ., Leningrad). Photochem. Photobiol.
4(3), 505-9 (1965)(Eng). Solns. of lumiflavine and riboflavine in
the presence of Ph_2NH show, under flash excitation, a reversible fading
of their absorption bands, with the appearance of bands of the semi-
quinone of the flavine and the cation radical of Ph_2NH; lumichrome
under similar conditions extracts a H atom from Ph_2NH.

Uspenskaya, V.E.　　　　　　　　　　　　　　2, 13
　　　　　　　　　　　　　　　　　　　　　　CA 63-6035c (1965)

Porphyrin pigments of green sulfur bacteria. (M.V. Lomonosov State
Univ., Moscow). Dokl. Akad. Nauk SSSR 162(4), 940-3 (1965)(Russ).

Vartanyan, A. T.   1, 13
                                                    CA 50-16393e (1956)

Absorption spectra of sublimed dye layers. Zhur. Fiz. Khim. 30,
1028-43 (1956)

Weigl, John W. and Livingston, Robert   14, 17

Infrared spectra of chlorophyll and related compounds. Journal of
American Chemical Society, Vol. LXXV (1953) p. 2173-6..

Weiss, Charles, Kobayashi, Hiroshi, and   10, 2
     Gouterman, Martin   CA 63-9229g (1965)

Spectra of porphyrins. III. Self-consistent molecular orbital
calculations of porphyrin and related ring systems. (Harvard Univ.).
J. Mol. Spectry. 16(2), 415-50 (1965)(Eng); cf. CA 59, 10451d.
S.C.M.O. calculations on the porphin ring by the method of Pariser,
Parr, and Pople (Pariser and Parr, CA 47, 1018f; Pople, CA 59, 5956h)
confirm earlier conclusions of Gouterman (CA 53, 16690b) and Platt (CA
47, 6251i) that the visible and Soret bands of the porphin absorption
spectrum can be explained by a four-orbital model. According to this
model, the lowest two pairs of excited configurations are accidentally
degenerate, and the extensive interaction between them accounts for
the great intensity of the Soret and the relative weakness of the
visible bands; interaction with higher configurations is negligible.
The four-orbital model is extended to give a successful account of
the absorption spectra of tetrabenzporphin, and of reduced and co-
porphyrins. It also accounts for the cyclic polyene perturbation
which splits the visible but not the Soret bands of free base porphin.
More elaborate calculations using extensive configuration interaction
give remarkable qualitative agreement with the porphin triplet-triplet
absorption spectrum, and make possible the reassignment of the ultra-
violet bands of tetrazaporphin and 90% of the total energy radiated by
the continuum. The spectral distribution of the continuum is integrated
to obtain a measurement of the total continuum energy radiated from N.
These are compared with direct measurements of the total radiation and
with a no. of theoretical predictions. These comparisons indicate that
at. line radiation is not an important contributor to the total radiation
for the conditions under investigation and that another source of
continuum radiation such as the neg. N ion may be an important contri-
butor in the visible region of the spectrum. Elec. and thermal conds.
of N and Ar plasma were also measured over this temp. range at atm.
pressure. Theory and other expts. are compared. From Nucl. Sci. Abstr.
19(8), 1787 (1965).

Whalley, Margaret \qquad 1, 4

Conjugated macrocycles. XXXII. Absorption spectra of tetrazaporphines and phthalocyanines. Formation of pyridine salts. (Inp. Coll., London). J. Chem. Soc. 1961, 866-9; CA 53, 6245h.

Williams, R. J. P. \qquad 2

The properties of metalloporphyrins. (Oxford Univ., Engl.). Chem. Revs. 56, 299-328 (1956). A review with 101 references.

Yagi, Kunio, Okuda, Jun, and Matsubara, Toshiro 8

Fatty acid esters of flavines. II. Riboflavine tetracaprate and riboflavine tetrabutyrate. (Univ. Nagoya, Japan). Bitamin (Kyoto) 21(4), 525-7 (1960); cf. ibid. 21(2), 217-20 (1960); ibid. 22(2), 175-7 (1961); CA 62, 855h. Riboflavine caprate and butyrate were prepd. The absorption spectra and fluorescence emission spectra of their alc. solns. were estd., and their R_f values in various solvents were also obtained. Chem. structure was studied by the estn. of riboflavine and fatty acid in the mols., and by periodate oxidn. These 2 derivs. are riboflavine 2', 3', 4', 5'-tetracaprate and riboflavine 2', 3', 4', 5'-tetrabutyrate.

Yonetani, Takashi \qquad 5, 1

Cytochrome oxidase. I. Absolute and difference absorption spectra. (Univ. of Pennsylvania, Philadelphia). J. Biol. Chem. 235, 845-52 (1960); cf. CA 53, 20146d. A purified prepn. of cytochrome oxidase was made by a modification of the method of Okunuki, et al. (CA 53, 4369c). The absorption spectra of the prepn. treated with cyanide, CO, and reducing agents are essentially in agreement with those of others. The possible reactions of cytochromes a and a_3 with cyanide, CO, and reducing agents, which are adapted to the detn. of difference spectra of cytochromes a and a_3 are considered. Cytochromes a and a_3 are spectrophotometrically sepd. from each other in the difference spectra, the results of which prove that about half of the peak at 445 $m\mu$ in the difference spectrum of cytochromes a and a_3 is due to oxidized cytochrome a, while the other half is due to reduced cytochrome a_3. The sepd. spectrum of reduced cytochrome a_3-CN show clear max. at 444 $m\mu$ and 590 $m\mu$. The sepd. spectra of reduced cytochrome

a_3-CO show max. at 430 mμ, 545 mμ, and 590 mμ, which are almost identical to those of the photochem. action spectra of the CO compd. of respiratory enzyme. The relation between cytochrome oxidase and cytochromes a and a_3 is discussed.

Zerner, Michael, and Gouterman, Martin   10, 2

                                                CA 64-7385f (1966)

Porphyrins. IV. Extended Hueckel calculations on transition metal complexes. (Harvard Univ.). Theoret. Chim. Acta 4(1), 44-63 (1966) (Eng); cf. CA 63, 9229g. The extended Hueckel model is applied to porphyrin systems with metals Mn, Fe, Co, Ni, Cu, Zn and to the diprotic acid. A single method for choosing parameters is detailed. The model is used to discuss magnetic state, coupling of ring and metal, electronic transitions, and the effect of nonplanarity.